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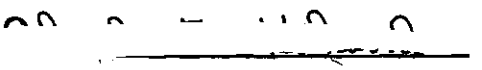

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POLYNUCLEAR COMPLEXES OF SOME FIRST ROW TRANSITION METALS

A THESIS

Presented to

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Studies and Research

By

Charles Edward Kirkwood

In Partial Fulfillment

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POLYNUCLEAR COMPLEXES OF SOME FIRST ROW TRANSITION METALS

Approved:

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SUMMARY

The single-crystal X-ray structure of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ is reported in this thesis; also the complex $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ was shown to be completely isostructural with the cobalt complex, and through a joint study with Bell Laboratories (28) the magnetic properties of the nickel cubane as a function of temperature are reported here. Also the single-crystal X-ray structure of $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$ is reported; this structure resembles the above two cubanes, but the acetylacetonate rings are disordered.

In these cubanes the four metal ions of one molecule form a tetrahedron; a methoxide ion is located over each face of the tetrahedron with the methoxide oxygen approximately equidistant from the three metal ions defining the face. The two oxygens of a pentanedionato group and the oxygen of a methanol or water complete the slightly distorted octahedral coordination of the metal ions. The temperature dependent magnetic studies of the nickel cubane indicate that the eight e_g electrons centered on the nickel tetramer are ferromagnetically coupled; the ground molecular spin state for the tetramer is $S' = 4$, and the ground state is fully populated at 21°K. At even lower temperatures μ_{eff} continues to increase; this indicates that the tetramer molecules in their ground state exhibit an additional intermolecular ferromagnetic coupling.

This complex provides the first example of a cluster complex

found to exhibit both intramolecular and intermolecular ferromagnetic spin coupling.

The effect of varying the metal ion and ligand in polynuclear complexes has been investigated. The ethanolimine ligand, EIA, produces an additional steric restraint on the complexes that is not present in the acetylacetone-methoxide cubanes. The complex, $[Co(EIA)]_4$, prepared in this work, was found to be isostructural with the previously reported cubane, $[Cu(EIA)]_4$. The X-ray structure of $[Ni(EIA)]_2$ is presented here. The structure of $[Ni(EIA)]_2$ consists of oxygen-bridged dimers with square-planar coordination about the nickel; the four-membered nickel-oxygen ring is considerably bent. With the ethanolimine ligand it is impossible to have a planar four-membered metal-oxygen ring and square-planar coordination of the metal.

In order to investigate further the effect of factors such as ring size and the extent of delocalization on the structure and magnetic properties, a complex, $[Cu(C_8H_{10}N_2O)]_2$, was prepared with a five-membered unsaturated ring. The compound is a planar dimer with a low magnetic moment of 0.54 B.M. A possible semi-quantitative explanation of the low moment is proposed. The explanation utilizes the O-M-O angle of the planar four-membered metal-oxygen ring to explain the lowering of the moment through the $p\pi$-$d\pi$ system of the metal-oxygen ring.

CHAPTER I

INTRODUCTION

Oxygen bridged complexes of the first transition series have many special features; these include the types of complexes formed, the chemical properties and the magnetic properties of these complexes. Within the past few years, chemists have become increasingly aware of the use of magnetic properties both as an aid in the understanding of chemical properties and as a tool to predict structural information. Since the magnetic properties of magnetically dilute systems have been investigated and are fairly well understood, the measurement of magnetic susceptibilities can at present provide valuable information on the oxidation states and stereochemistry of transition metal elements in such systems (1).

Lattice systems with strong ferromagnetic and antiferromagnetic tendencies have been studied extensively (2) and their properties are well known; however, the origin of these interactions is not understood on an atomic level. There is an intermediate type of system where interaction takes place among only a few magnetic dipoles; this behavior arises mainly in polynuclear complexes. These systems are not infinite and are simple enough that it should be possible through structural studies of a sufficient number of examples to develope an understanding of the magnetic interaction. Although some recent research has been devoted to the study of the magnetic properties of polynuclear

materials, some major aspects of these systems need further study, such as the pathway by which magnetic exchange is accomplished. More specific knowledge of the magnetic and structural properties of polynuclear compounds is needed before this field can be elucidated. The comparison of theory with experimental results is often hampered by a lack of stereochemical and structural knowledge of the system involved, i.e., unknown coordination numbers, unknown coordination symmetry, unknown stereochemistry of the bridging oxygens, unknown number of bridges between adjacent metal ions and unknown degree of polymerization. Due to these variables, there are a variety of structures possible for oxygen bridged complexes.

The magnetic properties of polynuclear complexes are of particular interest due to several possible types of magnetic interactions within these complexes. In order to understand the relationship between structure and magnetic properties, it is necessary to carry out complete single crystal X-ray structure determinations and temperature dependent magnetic studies of a number of complexes which differ in coordination numbers, coordination symmetry, stereochemistry of the bridging oxygens, number of oxygen bridges and degree of polymerization.

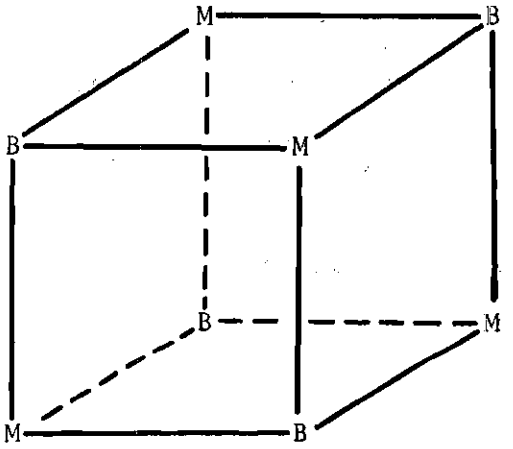
The geometry around oxygen may be tetrahedral (sp^3 hybridized), pyramidal (sp^3 hybridized with a lone pair of electrons), planar-triangular (sp^2 hybridized), bent (sp^3 or sp^2 hybridized) or linear (sp hybridized) depending on the number of groups attached to the oxygen and the use of the oxygen orbitals. Examples of all of these have been observed with metal ions of the first transition series; some of these

will be discussed to show the wide variety of oxygen bridged complexes possible.

Tetrahedral coordination of the oxygen by four metals is found in the μ_4-oxo complexes (3) in which a tetrahedron of metal ions surrounds an oxide ion; additional bridging groups span pairs of metal ions and are located above the six edges of the tetrahedron. Complexes with carboxylate ions as bridging groups have been prepared for divalent beryllium (4), zinc (5) and cobalt (6); the metal ions are tetrahedrally coordinated in these complexes. The cobalt complex has a magnetic moment, 3.86 B.M., considerably below the spin-only value for a tetrahedral cobalt(II) complex with three unpaired electrons, 4.4-4.8 B.M. A series of complexes of the general formula $M_4OB_6L_4$ have been reported for copper(II): the bridging, B, groups are halide ions and the L groups, representing triphenylphosphine oxide (7,8), pyridine (9), pyridine oxide (3), ammonia (3), chloride (10) or 2-methylpyridine (11), complete the trigonal-bipyramidal coordination of each copper. The room temperature magnetic moments of these complexes are normal, but a low temperature study (28) of the chloride-bridged triphenylphosphine oxide indicated a possible ferromagnetic interaction (down to 55°K) and antiferromagnetic (below 55°K) interactions; since the metal-metal distance is over 3.0Å, indirect interactions seem probable. The ferromagnetic interaction has been questioned by recent work (12). A magnesium complex $Mg_4OBr_6(Et_2O)_4$, similar to the above complexes has been prepared (13).

There is another type of compound in addition to the μ_4-oxo in

which the oxygen is tetrahedrally coordinated, although not by four metal ions; this compound can be referred to as a cubane-type complex (1).



1

In these compounds the tetrahedral alkoxide oxygen is bonded to the carbon of an alkyl group and coordinated to three metal ions; the structure can be described as a tetrahedron of metal ions, M, with bridging groups, B, above each face of the tetrahedron. The structure can alternately be described as two tetrahedra interpenetrating to form a cube, one tetrahedron of metals and the other of oxygens. Although this investigation will deal only with oxygen as the bridging group, this cubane-type complex has been observed for iodide-bridged complexes

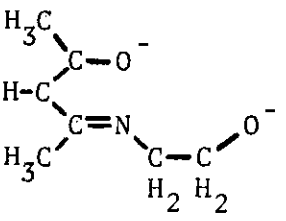
(14), ($[CuIL]_4$ where L represents tertiary phosphines and arsines); it has been suggested for sulfur bridged complexes (15) such as $[Zn(Et)(t\text{-}Bu\text{-}S)]_4$ and an aluminum-nitrogen cubane has been reported (16,70,86).

Before the start of this work cubane structures had been suggested for the methoxide complexes of the general formula $[M(AA)(OCH_3)(ROH)]_4$ (where M represents cobalt(II), nickel(II) or magnesium(II); AA represents the anion of acetylacetone, salicylaldehyde or o-hydroxyacetophenone (17); and R represents an alkyl group). There was need for the refinement of a complete single crystal X-ray structure of the cubane type in order that the structural details could hopefully be combined with a thorough low temperature magnetic investigation.

Structures of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$, $[Co(C_5H_7O_2)(OCH_3)(H_2O]_4$ and $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ are presented in this thesis. Through a joint study with Bell Laboratories, the magnetic results of a low temperature investigation of $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ can be presented along with the structure (18). While this work was in progress the cubane structure of $[Ni(sal)(OCH_3)(C_2H_5OH)]_4$, where sal represents the anion of salicylaldehyde, was published (19).

An earlier N.M.R. investigation by Bertrand and Caine (17) seemed to indicate that at room temperature the ligand groups attached to the magnesium cubane group interconverted rapidly between different isomeric forms in solution. Recent work (20) has shown that the magnesium cubane complex mentioned earlier disproportionates in dichloromethane to give magnesium(II) methoxide and magnesium(II)

acetylacetonate dihydrate; the latter compound is characterized in this thesis. It was thought at the beginning of this work that by varying the conditions of preparation and the method of crystallization that it should be possible to isolate different geometric isomeric forms in the solid crystalline state and that subsequent structure investigation of these isomers would prove interesting. If the alcohol is removed from these cubane complexes by drying in a vacuum, the complexes are assumed to have cubane structures with five-coordinate metal ions. A similar five-coordinate structure for $[Co(EIA)]_4$ is reported in this thesis, where EIA (2) represents the dianion of the imine formed from acetylacetone and 2-aminoethanol.



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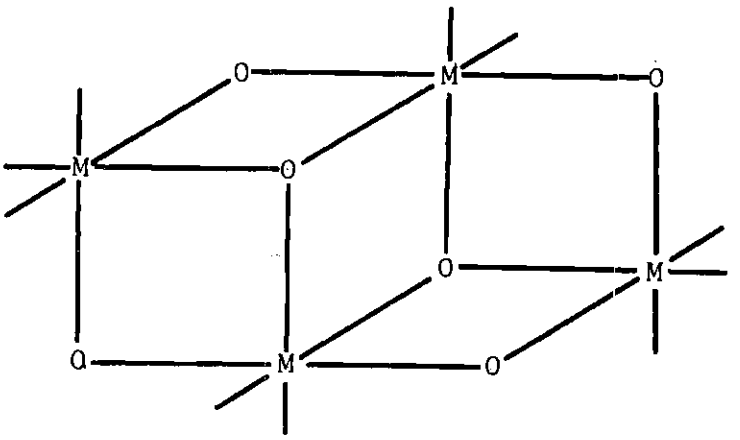
Later PIA will be used to represent the similar dianion formed from acetylacetonate and 3-amino-1-propanol.

Interesting compounds have resulted from varying the chemical and steric factors in complexes of this type; it has been found that by varying the metal by only one atomic number or by varying the ligand by only one carbon atom in the amino-alcohol portion of the chain (3) that the complexes formed may differ markedly. Kelley (3) obtained a tetrameric copper complex, $[Cu(EIA)]_4$, with EIA but obtained a dimeric

copper complex, $[Cu(PIA)]_2$, with PIA. It may even be possible that for particular complexes of this type that a dimer-tetramer change may be brought about in solution by changing the temperature only a few degrees. For one complex of such a system, $[Ni(EIA)]_2$, the X-ray crystal structure is presented in this thesis.

Another type of polynuclear complex consists of oxygens bridged in such a way as to form a displaced-dimer type of structure (3). This type of structure has been observed for several titanium(IV) alkoxides (21,22,23); the structure contains two μ_3-oxygens and four μ_2-oxygens. The remaining alkoxide groups are terminal and complete the octahedral coordination of the titanium(IV) ions.



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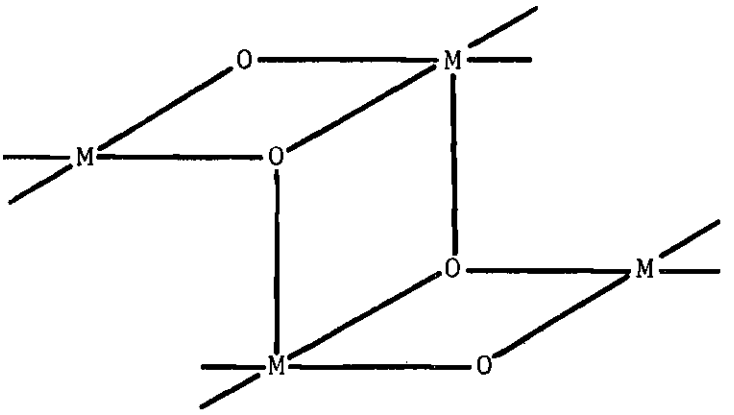
A similar structure has been observed for some copper(II) complexes. In the o-hydroxyanil copper(II) complex (4) there are two μ_2-oxygens; this structure differs from the previous structure in the number of μ_2-bridges -- the oxygen of the acetylacetone portion of the ligand (5) is not coordinated (24).



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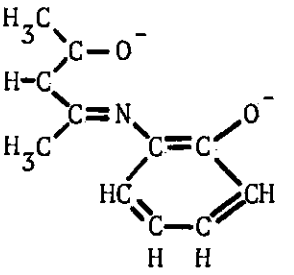

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The magnetic moment of the copper(II) ions of the tetramer, 1.37 B.M., indicates considerable interaction and a study (25) of the temperature dependence of the magnetic susceptibility indicates that the greatest exchange occurs between copper ions bridged by μ_2-oxygens. The same type of structure (26) has been found for the compound $[Cu(C_5H_7O_2)(OCH_2\text{-}C_6H_5)]_4$. A similar structure was found (27) for $[Cu_4(OH)_4(CH_3NH_2)_8(H_2O)_2]$; the coordination of the waters makes all copper(II) ions five coordinate. The four-membered ring is nonplanar in the latter compound and the Cu-Cu distance is 2.78Å.

A planar-triangular arrangement of groups about oxygen is found in the μ_3-oxo complexes. Complexes with the formula $M_3O(Ac)_6^+$ have been isolated (29,30) for iron(III) and chromium(III) and consist of an oxide ion at the center of an equilateral triangle of metal ions with two acetates bridging each edge of the triangle. Magnetic studies (2) of these complexes show an antiferromagnetic interaction at room temperature and at lower temperatures. The planar coordination of

oxygen indicates that one p-orbital of oxygen is not involved in σ-bonding and a four-center π-interaction between the metal ions and the central oxygen is possible.

There are at present several oxygen bridged dimeric complexes known. However, for most of these complete magnetic and structure information is not available.

An example of a linear arrangement of groups bonded to oxygen (31) is found in $Ru_2OCl_{10}^{-4}$. In the first transition series this linear arrangement has been observed (32,33) for some iron(II) complexes.

It is also possible to have complexes in which there is a four-membered metal-oxygen ring; the ring may be bent or planar. Although a large number of copper(II) compounds are associated into dimers and higher polymers through oxygen bridges, relatively few nickel(II) compounds with oxygen bridges have been reported; dimeric (34) $Ni(bdhe)ClO_4$ (where bdhe represents the anion of NN-bis-(2-diethylaminoethyl)-2-hydroxyethylamine) is an example of this type compound for which a structure has been reported. At the time this work was started there was no example of a four-membered bent ring in the first transition series; $[Ni(EIA)]_2$ is reported in this thesis as such an example. Another example of a bent ring appeared recently in the literature (35) for di-μ-hydroxybis(bipyridyl)dicopper(II) sulfate pentahydrate. $[Cu(PyO)_2Cl_2]_2$ can be quoted as an example of a copper four-membered planar metal-oxygen ring.

The atoms coordinated to the bridging oxygen may be oriented such that the oxygen is in the same plane or they may be oriented

such that the oxygen is out of the plane. Although magnetic moments have been correlated with these structural features, there is a definite need for additional X-ray structures combined with magnetic studies of these complexes. In this connection the X-ray structure and magnetic moment of $[Cu(C_8H_{10}N_2O)]_2$ are reported in this thesis.

In the course of studying polynuclear complexes, interest was aroused in some that were not polynuclear but were closely related to other complexes studied. Sometimes the same ligand may function either as a bridging group or as a chelate group on a metal; examples of a monomeric square planar nickel complex and a possible monomeric octahedral nickel complex are briefly investigated.

CHAPTER II

EXPERIMENTAL

Preparation of Complexes

Cobalt(II) Complex of the Dianion of the 1:1 Schiff's Base of Acetylacetone and 2-Aminoethanol, $[Co(EIA)]_4$ (36)

The Schiff's base of acetylacetone, $(CH_3CO)_2CH_2$, and 2-aminoethanol, $HOCH_2CH_2NH_2$, was prepared and isolated by the addition of 2-aminoethanol to an equimolar amount of acetylacetone. Equimolar amounts (0.02 mole) of the ligand and anhydrous cobalt(II) acetate were dissolved in absolute methanol and a solution made by dissolving sodium (0.04 mole) in methanol was added. Crystals of $[Co(EIA)]_4$ formed from the solution over several days. The dried crystals were stable only a few hours in air. The crystals were too unstable to obtain an elemental analysis. The proposed formula and structure of this complex was firmed by comparison of the X-ray powder diffraction pattern of this complex with that of $[Cu(EIA)]_4$ (36). Because the diffraction patterns are identical the compounds are isostructural.

Cobalt Complex of Diethanolamine, Methoxide and Iodide, $Co_2(C_4H_{10}NO_2)_3(OCH_3)I$

This compound was prepared by a variation of the method of Hieber and Levy (37). Anhydrous cobalt(II) iodide (0.01 mole) was dissolved in 100 ml of alcohol. A second solution of diethanolamine ($HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH$, 0.03 mole) dissolved in 100 ml of alcohol was prepared. The two solutions were added simultaneously from dropping funnels into a

third vessel containing 100 ml of boiling alcohol. The resulting solution was boiled down to 250 ml, filtered while hot, and allowed to cool. While cooling small green crystals formed.

Anal. Calcd. for $Co_2C_{13}H_{33}N_3O_7I$: C, 26.54; H, 5.65; N, 7.14.

Found: C, 26.21; H, 5.51; N,6.96.

Cubane Methoxo Derivative of Cobalt(II) Acetylacetonate with Terminal Methanol Groups, $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$

This complex was originally prepared by Bertrand and Kaplan (18,38). Crystals of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ were prepared by the addition of potassium hydroxide (0.01 mole), dissolved in 25 ml of methanol, to a refluxing methanol solution of cobalt(II) acetylacetonate (0.01 mole in 50 ml). The red crystals which separated from the refluxing solution were filtered and dried.

Anal. Calcd. for $CoC_7H_{14}O_4$: C, 38.0; H,6.3.

Found: C, 38.0; H, 5.7.

Cubane Methoxo Derivative of Cobalt(II) Acetylacetonate with Terminal Waters, $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$

Oxygen was removed from all methanol used in this reaction by passing nitrogen into the solvent before and during the preparation. Anhydrous cobalt(II) acetylacetonate (0.01 mole) was dissolved in deaerated methanol (200 ml). This solution was then cooled to dry ice temperature (-56.6°C) and a cold solution of potassium hydroxide (0.01 mole) dissolved in methanol (15 ml) was added. The resulting solution was kept at dry ice temperature for one hour. The solution was then transferred to a water-ice bath and as the ice melted, over a time of approximately 12 hours, the solution slowly warmed to room temperature

and red crystals suitable for single crystal X-ray work were formed. These crystals were identified as $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$ by a complete X-ray structure determination.

Copper(II) Complex of 3-Amino-1-propoxide and Acetate, $Cu(NH_2CH_2CH_2CH_2O)(CH_3CO_2)$

This complex was prepared by Bertrand by mixing equimolar amounts of copper(II) acetate monohydrate and 3-amino-1-propanol. To the above mixture methanol was added and purple needle-like crystals were obtained. The compound was characterized by the X-ray determined molecular weight.

Copper(II) Complex of the Dianion of the 1:1 Schiff's Base of Pyrrole-2-carboxaldehyde and 3-Amino-1-propanol, $[Cu(C_8H_{10}N_2O)]_2$

The compound 3-amino-1-propanol (0.005 mole, 0.38 grams) was added to pyrrole-2-carboxaldehyde (0.005 mole, 0.48 grams) and the mixture was dissolved in ten ml of methyl alcohol. The above solution and a solution containing potassium hydroxide (0.005 mole, 0.24 grams of approximately 85 per cent purity in 50 ml of methyl alcohol) were added simultaneously from dropping funnels with stirring to a warm cupric acetate solution (0.005 mole, 1.00 grams of $Cu(C_2H_3O_2)_2 \cdot H_2O$ in 100 ml of methyl alcohol).

A red-brown powder started to precipitate from the reaction mixture before the addition was complete; the product was filtered, washed and dried. In searching for a recrystallization solvent the compound was found to be insoluble in: acetone, carbon tetrachloride, acetonitrile, 2-methyl-1-propanol, nitromethane, toluene, water, and all xylenes. In the attempt to grow crystals suitable for single

crystal X-ray work, dimethyl sulfoxide was tried. All crystals grown from dimethyl sulfoxide were box-like needles or V-shaped needles. None could be successfully cleaved to obtain a good single crystal. The crystals used for the chemical analysis and for the X-ray structure determination were obtained from nitrobenzene. Well-formed red needle crystals were grown from this solvent; most were not single crystals but contained a fault line down the needle axis. One crystal was found that by optical examination appeared to be single and this was later confirmed by the successful completion of the structure.

Anal. Calcd. for $CuC_8H_{10}N_2O$: C, 44.96; H, 4.72; N, 13.11.
Found: C, 44.57; H, 5.05; N, 12.93.

Dihydrate of Magnesium(II) Acetylacetonate, $Mg(C_5H_7O_2)_2 \cdot 2H_2O$

The crystals used in this work were supplied by San Filippo (20). They were prepared in the following way. First $Mg(C_5H_7O_2)_2$ was prepared by adding freshly cut magnesium ribbon to excess acetylacetone and allowing this to stand for 48 hours. This white compound was isolated, recrystallized from methanol, and then dried in a vacuum desiccator over concentrated sulfuric acid. The methoxo derivative was prepared by the method of Bertrand and Caine (17), the white crystals of $Mg(C_5H_7O_2)(OCH_3)(CH_3OH)$ were isolated and dried over concentrated sulfuric acid. An attempt was made to recrystallize this complex from dichloromethane and colorless, clear needle crystals of $Mg(C_5H_7O_2)_2 \cdot 2H_2O$ were obtained. This formulation for the complex was substantiated by a molecular weight determination by X-ray methods and by an elemental analysis. The experimental X-ray molecular weight is

255 and the calculated molecular weight is 258.

Anal. Calcd. for $MgC_{10}H_{18}O_6$: C, 46.45; H, 7.02.

Found: C, 46.27; H, 7.15.

Cubane Methoxo Derivative of Nickel(II) Acetylacetonate, $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ (18)

Method One. This method was reported by Bertrand and Kaplan (38). Nickel(II) acetylacetonate ($Ni(C_5H_7O_2)_2$, 0.007 mole) was dissolved in 350 ml of refluxing methanol. Potassium hydroxide (0.007 mole) in methanol was added dropwise to the refluxing solution over a period of one hour. After two hours at reflux, the solution was filtered while hot. Large green crystals of the complex separated as the filtrate cooled.

Anal. Calcd. for $NiC_7H_{14}O_4$: C, 38.0; H, 6.3.

Found: C, 38.8; H, 5.8.

Method Two. The following preparation -- which was used to obtain crystals for single crystal X-ray work -- was discovered by accident while trying to prepare $Ni(PIA)(CH_3OH)$. PIA is used here and elsewhere to represent the dianion of the Schiff's base of acetylacetone and 3-amino-1-propanol. The white imine of 3-amino-1-propanol and acetylacetone was formed by mixing equimolar (0.005 mole) quantities of each in a dry flask. The imine formed was dissolved in 100 ml of methanol with medium heat and with stirring. Then nickel(II) acetylacetonate (0.005 mole) was added to the above solution with further heat and stirring. Finally a solution formed by reacting sodium (0.01 mole) with methanol (150 ml) was added slowly from a dropping funnel to the above solution. The resulting solution was filtered while hot.

This preparation either gave crystals with the shape of two irregular hexagons joined together to form a V-shape or gave green triangular needles that were very good for single crystal X-ray work. These crystals were stable for up to several days but were not stable indefinitely in air.

Anal. Calcd. for $NiC_7H_{14}O_4$ (Method Two): C, 38.0; H, 6.3.
Found: C, 41.3; H, 6.4.

Ethanolate of a Nickel(II) Complex of the Dianion of the 1:1 Schiff's Base of Salicylaldehyde and 3-Amino-1-propanol, $Ni(C_{10}H_{11}NO_2)(C_2H_5OH)$

This compound was prepared by a modification of the method of Breece (39). J. L. Breece prepared a green crystalline compound without the use of sodium ethoxide. In the preparation reported here a solution containing the imine of 3-amino-1-propanol and salicylaldehyde was prepared by mixing equimolar (0.01 mole) amounts of the compounds in ethanol (100 ml). A second solution was prepared by reacting sodium metal (0.01 mole) with ethanol (100 ml). The two solutions were slowly added simultaneously from dropping funnels to a boiling solution of anhydrous nickel(II) acetate (0.01 mole) in ethanol (300 ml). A light green powder precipitated from the boiling solution during the latter part of the addition.

Anal. Calcd. for $NiC_{12}H_{17}NO_3$: C, 51.10; H, 6.08; N, 4.96.
Found: C, 50.65; H, 5.97; N, 4.95.

Nickel(II) Complex of the Dianion of the 1:1 Schiff's Base of Salicylaldehyde and 3-amino-1-propanol, $Ni(C_{10}H_{11}NO_2)$

If $Ni(C_{10}H_{11}NO_2)(C_2H_5OH)$ is added to m-xylene at room temperature it forms a green solution. When this solution is heated the color

gradually changes to red-brown. Green $Ni(C_{10}H_{11}NO_2)(C_2H_5OH)$ was added to anhydrous m-xylene and the solution boiled. Some m-xylene was allowed to evaporate in order to saturate the solution with the red-brown compound. The solution was allowed to cool to a temperature slightly above room temperature where the solution retained its red-brown color; the red-brown crystals were allowed to form at this temperature. These crystals were filtered off in an apparatus in which the funnel was kept hot through the use of electrical heating tape. They were washed with boiling m-xylene. Many green crystals were present along with the red-brown compound at this point. This batch of crystals was added to more anhydrous m-xylene and the boiling, precipitation and hot filtration was repeated. This time a product was obtained which contained, by sight, an estimated 99 per cent of the red-brown crystals and only 1 per cent of the green compound. The following nickel analysis is described latter in this chapter.

Anal. Calcd. for $NiC_{10}H_{11}NO_2$: Ni, 24.89; C, 50.89; H, 4.71; N, 5.94.

Found: Ni, 24.83; C, 51.0; H, 4.47; N, 5.88.

Methanolate of a Nickel(II) Complex of the Dianion of the 1:1 Schiff's Base of Acetylacetone and 2-Aminoethanol, $Ni(EIA)(CH_3OH)$

The method of Jager (40) was used to prepare the methanolate, $Ni(EIA)(CH_3OH)$. It was found that crystals suitable for single crystal X-ray work could be obtained only by the following procedure. The Schiff's base of acetylacetone, $(CH_3CO)_2CH_2$, and 2-aminoethanol, $HOCH_2CH_2NH_2$, was prepared and isolated. Twenty-five grams of acetylacetone were dissolved in 200 ml of toluene. This solution was heated

and 15 grams of 2-aminoethanol were added. This reaction mixture was refluxed for several hours in the bottom of a Soxhlet apparatus with aluminum oxide, Al_2O_3, in the thimble section. The purpose of the aluminum oxide was to remove all of the water present. The colorless crystals of the ligand, $C_7H_{13}NO$, precipitated while cooling the solution. Equimolar amounts of the ligand (0.005 mole) and water-free nickel acetate ($Ni(C_2H_3O_2)_2$, 0.005 mole) were dissolved in absolute methanol (250 ml). The nickel acetate had been previously dried under vacuum at 80°C; and the methanol dried over anhydrous sodium sulfate, Na_2SO_4. To the above warmed and stirred solution a solution of sodium (0.01 mole) in absolute methanol (50 ml) was added from a dropping funnel. Green crystals were then formed which appeared to be stable indefinitely in contact with solution and sometimes stable for as long as several days in the air. It was found that well-formed crystals for X-ray work could be formed at the above concentrations.

Anal. Calcd. for $NiC_8H_{15}NO_2$: C, 41.42; H, 6.53; N, 6.04.
Found: C, 41.21; H, 7.13; N, 5.77.

Nickel(II) Complex of the Dianion of the 1:1 Schiff's Base of Acetylacetone and 2-Aminoethanol, $[Ni(EIA)]_2$ (41)

Red crystals of $[Ni(EIA)]_2$ suitable for single crystal X-ray work were prepared from the green $Ni(EIA)(CH_3OH)$ complex by the following procedure. When a green, room temperature toluene solution of $Ni(EIA)(CH_3OH)$ was heated, the color gradually changed to red. Toluene was first dried over anhydrous calcium chloride, $CaCl_2$. The toluene was then refluxed for four hours in a Soxhlet apparatus with aluminum oxide in the thimble, and the $Ni(EIA)(CH_3OH)$ was added to the

boiling toluene in the Soxhlet extractor. After boiling one hour, the solution was filtered, and well-shaped red needle crystals had formed.

Anal. Calcd. for $NiC_7H_{11}NO$: C, 42.06; H, 5.56; N, 7.01.

Found: C, 42.22; H, 5.52; N, 6.93.

Nickel(II) Complex Prepared from Nickel Acetate, Ammonium Acetate, Potassium Nitrite and Acetylacetone, $NiC_{10}H_{14}N_4O_4$

This compound was prepared by the method of Djordjevic, Lewis and Nyholm (42). Nickel acetate tetrahydrate (10 g) in a water-alcohol mixture (two volumes water to one volume ethanol) containing ammonium acetate (50 g), was treated with potassium nitrite (90 g) in water (30 ml) and acetylacetone (9 ml). This was stirred at a lukewarm temperature for about three hours. The solid red material that formed was filtered off and dried for about one hour at 80°C. This dried powder was then reprecipitated from benzene; the precipitate was dissolved in nitromethane and filtered to remove any solid undissolved material. This solution was stoppered and placed in a drying oven at 61°C, and the temperature was lowered stepwise over two days until 40°C was obtained. After the temperature of the solution was held constant at 40°C for two days, well-formed red needle crystals suitable for single crystal X-ray work were formed.

Anal. Calcd. for $NiC_{10}H_{14}N_4O_4$: C, 38.38; H, 4.51; N, 17.90.

Found: C, 38.36; H, 4.54; N, 18.07.

Nickel(II) Complex of Triethanolamine and Chloride, $Ni(TEA)_2Cl_2$

In the above formula and elsewhere TEA is used to refer to triethanolamine, $N(CH_2CH_2OH)_3$. The above compound was prepared by the method of Hughes and Rutt (43). Blue crystals were prepared by the

addition of triethanolamine to an ethanol solution of nickel chloride hexahydrate in a two to one molar ratio.

Anal. Calcd. for $NiC_6H_{15}O_3Cl_2$: C, 33.6; H, 7.06; N, 6.54; Cl, 16.55.

Found: C, 33.8; H, 6.95; N, 6.52; Cl, 16.57.

Crystallographic Studies

Calculations

Computations were carried out on the Burroughs 5500 computer and on the Univac 1108 computer. Programs used included modified versions of Zalkin's FORDAP Fourier summation program (44); Busing, Martin and Levy's ORFLS (45), XFLS (46) and ORFFE (47): a program for calculating Lorentz-polarization corrections by Bertrand (48); two programs for calculating the least-squares plane for a set of atoms, one by Bertrand and Kelley (3) and one by Kalyanaraman (49); a data reduction program by the author (see Appendix); and Johnson's ORTEP (50) for drawing crystal structure illustrations.

Solution of the Structure of $[Cu(C_8H_{10}N_2O)]_2$

A red needle-like crystal with dimensions 0.10 x 0.11 x 0.39 mm was mounted on the precession camera with the long dimension, b, along the spindle axis. Viewed from the end, the crystal is a parallelogram with the acute angle equal to approximately 89.5°. Orientation precession photographs were taken, using zirconium-filtered Mo Kα radiation, λ = 0.7106Å. The crystal was found to be monoclinic with a = 25.61(2)Å, b = 5.46(1)Å, c = 16.90(2)Å and β = 136.33(10)°. The density calculated on the basis of four dimer units per unit cell,

1.74 g/cm^3, agrees well with the experimental value, 1.73(1) g/cm^3, obtained by the flotation method using a mixture of carbon tetrachloride and diiodomethane.

A zone located at a spindle setting of 4°42.5' was designated $hk0$; a zone located at a spindle setting of 48°42.5' was designated $0kl$. The absence of hkl reflections with $h + k = 2n + 1$ and the absence of $h0l$ reflections with $l = 2n + 1$ indicated space group Cc (No. 9) or C2/c (No. 15). The Patterson synthesis gave some evidence that the correct space group was C2/c. Due to their different symmetries, the strongest non-origin peaks in the Patterson should occur on the line $0,y,1/2$ for space group Cc but strong peaks of equal intensity should occur on the line $0,y,1/2$ and in the plane $x,0,z$ for space group C2/c ; the latter situation was observed in this case and this choice was confirmed by the successful refinement of the structure.

Intensity data were collected on the precession camera, using the same crystal as used for the space group determination. A total of 858 unique, non-zero reflections were estimated visually from the $hkl(l = 0$ to $-4)$ and the $hkl(h = 0$ to $6)$ layers. For both zero levels and for the $hkl(l = 1$ to $-4)$, three timed exposures of 100, 10.0 and 1.0 hours were made. For the $hkl(h = 1$ to $6)$ three timed exposures of 50, 10.0 and 1.0 hours were made. Ilford Industrial-G X-ray film was used. Lorentz and polarization corrections were computed but no corrections for absorption were made. The linear absorption coefficient, μ, was calculated to be 27 cm^{-1} using values of the atomic absorption coefficients given in the *International Tables for X-Ray*

Crystallography (51). The following formula was used to calculate μ

$$\mu = \frac{10}{V} \times N \times \Sigma(\mu_a \times A)$$

where V = volume of the unit cell, N = number of molecules per unit cell, μ_a = atomic absorption coefficient and A = number of these particular atoms in the formula.

The coordinates of the copper atom were determined from a three-dimensional Patterson synthesis. After three cycles of full-matrix least-squares refinement, the conventional R_1 value ($\Sigma||Fo| - |Fc|| / \Sigma|Fo|$) was 0.34. At this point, with all reflections weighted at unity, the value of R_2 ($\{\Sigma_i - (|Fo| - |Fc|)^2 / \Sigma_i w_i|Fo|)^2\}^{1/2}$) was 0.40; a Fourier synthesis revealed the positions of all nonhydrogen atoms. Full-matrix least-squares refinement of all atomic coordinates, individual isotropic thermal parameters and individual layer scale factors was continued until there was no parameter shift greater than 1/10 of one estimated standard deviation (esd). At this point, R_1 = 0.093 and R_2 = 0.090. The Fourier at this stage showed a definite anisotropic thermal motion of the copper atom. Anisotropic thermal parameters were assigned to copper. Further full-matrix refinement was carried out, followed by a difference Fourier synthesis. From this difference Fourier synthesis all hydrogen atoms were located. Some of the hydrogen atoms were placed slightly off the peak maximum where this improved chemical bond lengths and angles. Each hydrogen atom was assigned the isotropic temperature

factor of the adjacent carbon. Further refinement of all parameters except hydrogen coordinates and hydrogen temperature factors converged to $R_1 = 0.076$ and $R_2 = 0.076$. In the final cycle of refinement, no parameter showed any significant change; no shift was greater than 1/10 of one esd. Table 1 lists the final positional parameters derived from the last cycle. The anisotropic temperature factors are given in Table 2 , and Table 3 lists the observed and calculated structure factors. In the structure factor calculations, the scattering factors tabulated by Ibers (51) were employed for all atoms.

Table 1. Final Positional and Thermal Parameters for $[Cu(C_8H_{10}N_2O)]_2$

Atom	x	y	z	B, $Å^2$
Cu	0.2382(1)	0.0620(2)	0.0507(1)	2.2(1)
O	0.3139(4)	0.194(1)	0.0641(6)	2.4(1)
N1	0.1665(5)	-0.063(2)	0.0489(8)	2.9(2)
N2	0.3005(5)	-0.209(1)	0.1564(8)	2.7(2)
C1	0.3901(6)	0.108(2)	0.1389(9)	2.6(2)
C2	0.4185(5)	-0.014(2)	0.2468(9)	2.7(2)
C3	0.3792(6)	-0.253(2)	0.2182(9)	2.6(2)
C4	0.2668(6)	-0.342(2)	0.172(1)	2.7(2)
C5	0.1924(6)	-0.266(2)	0.111(1)	2.6(2)
C6	0.1401(6)	-0.365(2)	0.105(1)	3.2(2)
C7	0.0765(7)	-0.207(2)	0.035(1)	4.2(3)
C8	0.0967(6)	-0.023(2)	0.003(1)	3.6(3)
H1C1	0.397	-0.010	0.104	
H2C1	0.431	0.240	0.175	
H1C2	0.464	-0.060	0.323	
H2C2	0.400	0.100	0.275	
H1C3	0.380	-0.365	0.175	
H2C3	0.402	-0.332	0.289	
HC4	0.290	-0.500	0.230	
HC6	0.140	-0.520	0.140	
HC7	0.024	-0.200	0.001	
HC8	0.055	0.100	-0.058	

Table 2. Final Anisotropic Thermal Parameters ($\times 10^4$) for $[Cu(C_8H_{10}N_2O)]_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	16(1)	189(4)	47(1)	7(1)	17(1)	18(2)

Table 3. Observed and Calculated Structure Factors for $[Cu(C_8H_{10}N_2O)]_2$

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
	L= 0				L= -1			9	3	685	635	-1	7	157	167
								11	3	306	287	1	7	91	117
				-17	1	158	129	15	3	153	144	3	7	128	161
4	0	545	446	-15	1	346	363	17	3	183	165				
6	0	1839	1924	-13	1	396	428	19	3	94	107		L= -2		
8	0	901	844	-11	1	579	509	21	3	95	116				
10	0	300	352	-9	1	867	768	-20	4	258	284	-20	0	321	333
12	0	839	825	-7	1	680	638	-18	4	394	393	-18	0	329	332
14	0	743	667	-5	1	607	587	-16	4	298	308	-16	0	294	356
16	0	513	478	-3	1	927	842	-14	4	324	330	-14	0	973	898
18	0	323	306	5	1	528	463	-12	4	389	445	-12	0	1334	1344
3	1	378	348	7	1	245	266	-10	4	311	313	-10	0	1040	967
5	1	851	871	9	1	150	84	-8	4	264	256	-8	0	405	418
7	1	780	758	11	1	179	154	-6	4	211	207	-6	0	878	860
9	1	750	717	13	1	332	275	-2	4	206	181	-4	0	1421	1417
11	1	867	857	15	1	321	248	2	4	290	307	-2	0	1539	1586
13	1	1029	970	17	1	86	105	4	4	461	498	6	0	489	550
15	1	953	965	23	1	136	102	6	4	807	797	8	0	679	790
17	1	711	696	-22	2	291	259	8	4	771	766	10	0	636	666
19	1	347	445	-20	2	271	290	10	4	555	558	12	0	125	118
21	1	329	384	-18	2	283	265	12	4	553	574	14	0	139	139
23	1	283	303	-16	2	129	122	14	4	550	531	18	0	235	201
0	2	603	625	-14	2	150	156	16	4	494	484	20	0	325	305
2	2	489	533	-12	2	580	500	18	4	499	532	22	0	344	325
4	2	754	814	-10	2	408	447	20	4	457	483	24	0	319	295
6	2	1374	1313	-8	2	177	165	22	4	359	337	26	0	228	195
8	2	1130	1071	-6	2	118	119	-17	5	151	143	-19	1	317	301
10	2	802	855	-2	2	827	846	-15	5	160	116	-17	1	264	291
12	2	797	801	2	2	349	283	-13	5	162	171	-15	1	288	294
14	2	266	264	4	2	434	407	-11	5	397	428	-13	1	269	234
16	2	211	186	6	2	861	839	-9	5	589	639	-9	1	181	205
1	3	185	208	8	2	1006	1006	-7	5	523	554	-7	1	73	93
3	3	737	744	10	2	1020	992	-5	5	450	519	-5	1	720	681
5	3	603	557	12	2	908	836	-3	5	708	716	-3	1	312	354
7	3	92	90	14	2	632	583	-1	5	562	625	-1	1	439	373
9	3	270	214	16	2	366	368	1	5	386	411	1	1	2234	2317
13	3	126	78	18	2	340	324	3	5	562	596	3	1	1307	1380
15	3	225	163	20	2	377	398	5	5	708	731	5	1	619	618
17	3	171	154	22	2	253	248	7	5	551	590	7	1	1658	1706
19	3	76	102	-21	3	240	213	9	5	370	423	9	1	811	870
21	3	222	218	-19	3	285	264	11	5	263	224	11	1	720	763
0	4	278	302	-17	3	299	299	-12	6	126	129	13	1	1688	1563
8	4	270	297	-15	3	391	440	-10	6	159	197	15	1	1228	1221
10	4	232	284	-13	3	471	526	-8	6	186	175	17	1	594	547
3	5	224	215	-11	3	342	415	-6	6	132	134	19	1	503	458
5	5	374	406	-9	3	520	557	-2	6	133	121	21	1	477	437
7	5	199	209	-7	3	1229	1273	4	6	249	277	23	1	335	306
0	6	320	366	-5	3	1632	1531	6	6	266	239	25	1	255	237
2	6	320	358	-3	3	888	898	8	6	297	291	-20	2	196	181
4	6	225	241	-1	3	875	976	10	6	349	361	-18	2	158	130
6	6	211	177	1	3	1273	1336	12	6	226	240	-16	2	304	336
8	6	255	281	3	3	1236	1260	14	6	201	217	-14	2	560	521
10	6	203	190	5	3	1005	986	16	6	224	233	-12	2	386	413
12	6	96	87	7	3	727	706	-3	7	201	186	-10	2	703	706

Table 3. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-8	2	1076	1112	17	5	158	150	8	2	1310	1355	-3	5	362	356
-6	2	1008	959	21	5	108	134	10	2	1198	1275	-1	5	321	256
-4	2	1155	1142	-14	6	148	163	12	2	793	760	1	5	357	354
-2	2	1308	1418	-12	6	328	276	14	2	852	797	3	5	338	314
2	2	817	845	-10	6	248	227	16	2	911	912	5	5	159	124
6	2	258	258	-8	6	250	214	18	2	647	626	7	5	113	72
8	2	931	919	-6	6	388	417	20	2	307	303	9	5	114	112
10	2	236	179	-4	6	448	455	22	2	162	169	11	5	346	341
12	2	118	102	-2	6	336	312	-19	3	300	316	13	5	309	294
14	2	89	112	0	6	274	280	-17	3	363	380	15	5	118	129
16	2	286	299	2	6	296	269	-15	3	234	233	17	5	169	124
18	2	452	436	4	6	158	168	-13	3	338	350	19	5	209	219
20	2	150	139	10	6	224	190	-11	3	612	717	21	5	242	251
22	2	157	146	12	6	112	130	-9	3	925	854	23	5	168	175
24	2	196	180	-3	7	156	128	-7	3	939	904	-6	6	210	162
26	2	158	165	-1	7	272	275	-5	3	1123	1056	-4	6	271	276
-19	3	195	188	1	7	315	295	-3	3	912	826	-2	6	363	382
-17	3	158	163	3	7	295	277	-1	3	352	332	2	6	209	172
-15	3	243	264	5	7	315	271	1	3	227	154	4	6	362	355
-13	3	181	187	7	7	247	222	3	3	398	441	6	6	295	282
-11	3	142	151	9	7	290	251	5	3	513	450	8	6	120	125
-9	3	192	180	11	7	304	310	11	3	248	219	10	6	320	275
-7	3	92	73	13	7	233	249	13	3	138	123	12	6	364	382
-5	3	89	118	15	7	196	209	15	3	354	371	14	6	272	289
1	3	618	587					17	3	399	394	16	6	243	226
3	3	832	727		L=	-3		19	3	417	481	18	6	208	194
5	3	421	397					21	3	464	473	20	6	117	95
7	3	816	744	-17	1	164	210	23	3	360	380				
9	3	887	823	-15	1	330	363	25	3	273	270		L=	-4	
11	3	450	416	-13	1	291	322	27	3	171	160				
13	3	331	354	-11	1	270	283	-10	4	196	145	-16	0	314	399
15	3	315	311	-9	1	351	380	-8	4	331	313	-14	0	439	583
17	3	232	187	-7	1	226	260	-6	4	457	530	-12	0	999	1026
19	3	264	231	-5	1	226	254	-4	4	447	487	-10	0	838	916
21	3	157	150	-3	1	247	310	-2	4	413	372	-8	0	902	903
-8	4	178	94	-1	1	302	251	2	4	846	745	-6	0	1058	1113
-6	4	142	113	9	1	165	194	4	4	1011	1031	-4	0	726	680
-4	4	99	82	11	1	872	796	6	4	1364	1429	-2	0	647	746
4	4	136	158	13	1	736	666	8	4	1128	1160	10	0	1026	1079
8	4	171	179	15	1	85	165	10	4	876	788	12	0	551	525
12	4	177	133	17	1	132	132	12	4	524	556	14	0	1163	1124
16	4	241	212	19	1	100	130	14	4	290	263	16	0	1135	1126
22	4	158	95	21	1	153	135	16	4	318	283	18	0	887	910
-17	5	151	160	23	1	229	176	18	4	401	376	20	0	838	809
-9	5	110	119	25	1	120	170	20	4	291	282	22	0	523	562
-7	5	327	274	27	1	246	258	22	4	271	262	24	0	409	439
-1	5	184	176	-10	2	169	121	24	4	211	195	26	0	434	478
3	5	300	245	-8	2	204	188	-17	5	204	222	-13	1	304	366
5	5	369	415	-6	2	400	464	-15	5	296	296	-11	1	357	425
7	5	283	247	-4	2	708	664	-13	5	271	300	-9	1	368	368
9	5	323	282	-2	2	1030	1074	-11	5	340	341	-7	1	711	687
11	5	266	240	2	2	832	969	-9	5	411	383	-5	1	902	974
13	5	155	163	4	2	726	641	-7	5	438	383	-3	1	919	950
15	5	248	239	6	2	770	798	-5	5	433	414	-1	1	1522	1457

Table 3. (Continued)

H	K	FO	FC	H	K	FO	FC	K	L	FO	FC	K	L	FO	FC
9	1	1565	1684	-9	5	110	132	2	8	291	293	3	4	464	472
11	1	1612	1437	-7	5	216	188	2	10	526	513	3	5	158	125
13	1	991	1014	-5	5	320	283	2	11	153	177	3	6	282	223
15	1	912	892	-3	5	315	285	2	12	235	196	3	7	336	269
17	1	405	430	-1	5	180	148	2	13	248	246	3	8	122	159
21	1	187	180	1	5	178	194	2	14	108	110	3	9	503	438
23	1	141	169	3	5	290	273	4	1	158	169	3	11	455	437
-16	2	286	320	7	5	103	117	4	3	639	594	5	-11	127	186
-14	2	356	428	9	5	254	265	4	4	270	363	5	-9	391	421
-12	2	363	456	11	5	256	240	4	5	653	553	5	-7	183	184
-10	2	128	147	13	5	183	205	4	7	581	529	5	-5	128	41
-8	2	85	103	15	5	152	163	4	8	131	132	5	1	584	625
-6	2	612	554	17	5	109	102	4	9	243	237	5	2	189	176
-4	2	798	751	19	5	111	105	4	11	108	90	5	3	286	256
-2	2	693	626	-10	6	160	186	6	3	228	238	5	4	128	148
2	2	680	602	-8	6	160	184	6	5	318	367	5	6	225	233
4	2	324	241	-4	6	194	196	6	6	148	144	5	7	225	256
6	2	167	132	-2	6	193	216	6	7	161	186	5	9	366	368
8	2	526	495	6	6	111	82	6	8	154	194	5	11	121	184
10	2	565	463	14	6	159	107					7	1	123	167
12	2	198	180	16	6	160	169		H=	1		7	2	212	275
14	2	728	682	18	6	226	229					7	4	204	242
16	2	828	786	20	6	159	159	1	-14	327	367				
18	2	280	259	22	6	111	118	1	-12	492	534		H=	2	
20	2	284	298	-11	7	105	153	1	-11	211	235				
22	2	376	424	-9	7	155	128	1	-9	329	407	0	-12	707	746
24	2	237	238	-1	7	198	242	1	-8	564	558	0	-10	1093	1144
26	2	192	209	1	7	324	336	1	-7	570	561	0	-8	1498	1465
-7	3	241	228	3	7	257	269	1	-6	1898	1784	0	-6	643	715
-5	3	123	101	5	7	325	272	1	-5	116	92	0	-4	1779	1679
-3	3	342	337	7	7	324	324	1	-4	2390	2499	0	2	1749	1586
-1	3	561	472	9	7	256	242	1	-3	2066	2214	0	4	687	746
1	3	152	113	11	7	228	219	1	-1	117	97	0	6	221	206
3	3	234	211	13	7	197	219	1	0	117	164	0	8	958	974
5	3	295	349	15	7	112	138	1	2	375	373	0	10	703	658
7	3	398	363	17	7	111	119	1	3	291	251	0	12	197	153
9	3	719	621					1	4	1644	1457	0	14	250	183
11	3	305	349	K	L	FO	FC	1	5	445	377	2	-15	321	340
13	3	256	187		H=	0		1	6	1176	1123	2	-13	277	255
15	3	380	374					1	7	608	478	2	-12	232	250
17	3	133	157	0	2	2061	2035	1	8	978	863	2	-11	129	116
19	3	98	51	0	4	484	408	1	9	517	500	2	-10	326	413
21	3	252	167	0	6	519	526	1	11	335	264	2	-9	166	182
23	3	107	68	0	8	856	853	1	12	393	340	2	-8	796	761
-8	4	288	230	0	10	962	1036	1	14	422	359	2	-7	587	578
-6	4	297	265	0	12	347	398	3	-13	187	195	2	-6	856	775
-4	4	215	225	0	14	136	110	3	-11	447	470	2	-5	927	914
2	4	223	175	2	1	873	926	3	-9	474	475	2	-2	788	845
4	4	271	267	2	2	981	1050	3	-8	118	112	2	1	754	846
6	4	272	278	2	3	1263	1208	3	-7	365	408	2	2	1320	1418
8	4	275	229	2	4	884	873	3	-6	355	416	2	3	923	1074
10	4	93	63	2	5	653	652	3	-5	189	191	2	4	602	626
12	4	165	154	2	6	279	265	3	1	933	976	2	5	1013	1062
14	4	98	73	2	7	393	396	3	3	339	332	2	6	158	161

Table 3. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
2	7	643	610	1	11	354	297	2	-6	1293	1276	1	11	251	241
2	8	476	429	1	14	169	218	2	-5	1336	1278	3	-12	234	249
2	10	597	456	3	-13	162	187	2	2	1086	1142	3	-11	507	569
2	11	239	214	3	-11	306	321	2	3	717	664	3	-10	438	469
2	12	549	487	3	-9	538	543	2	4	809	751	3	-9	821	839
2	13	143	126	3	-8	311	280	2	5	1000	878	3	-7	595	667
4	-13	245	257	3	-7	406	446	2	6	141	152	3	-5	496	527
4	-11	197	210	3	-6	263	266	2	7	526	487	3	1	1514	1531
4	-8	133	136	3	-5	364	371	2	8	191	143	3	2	98	118
4	-7	261	258	3	1	891	898	2	10	416	340	3	3	1018	1056
4	-5	698	681	3	3	831	826	2	12	478	435	3	4	105	101
4	1	177	181	3	4	325	337	4	-13	308	299	3	5	153	150
4	3	402	372	3	6	429	446	4	-12	123	159	3	6	503	503
4	5	653	611	3	7	404	346	4	-11	171	208	3	7	451	375
4	7	604	579	3	8	373	346	4	-10	119	76	3	8	340	297
4	8	168	192	3	9	544	504	4	-8	229	187	3	9	512	470
4	9	279	237	3	11	286	246	4	-7	318	300	3	11	262	248
4	13	133	171	5	-11	286	295	4	-5	982	965	5	-11	317	279
6	-8	139	192	5	-9	432	405	4	3	502	487	5	-10	181	227
6	-7	198	266	5	-7	322	325	4	4	228	225	5	-9	506	536
6	-6	199	239	5	-6	226	194	4	5	736	776	5	-7	527	585
6	-5	346	393	5	1	791	716	4	7	593	528	5	-6	246	223
6	-2	245	269	5	3	391	356	4	9	251	227	5	-5	122	83
6	1	141	121	5	4	321	285	6	-10	180	146	5	-4	172	114
6	2	283	312	5	5	280	247	6	-9	128	121	5	1	523	519
6	3	316	382	5	6	283	248	6	-8	181	208	5	3	500	414
6	4	199	216	5	7	232	192	6	-7	256	271	5	4	309	283
6	5	372	365	5	9	286	287	6	-6	313	266	5	5	296	227
6	6	139	119	5	11	226	237	6	-5	404	397	5	9	264	261
				7	-6	229	202	6	2	478	455	5	11	183	257
	H= 3			7	1	164	186	6	3	286	276				
				7	6	187	257	6	4	181	196		H= 6		
1	-16	168	226					6	5	181	209				
1	-14	450	464		H= 4							0	-16	260	241
1	-13	108	140						H= 5			0	-14	165	155
1	-12	436	476	0	-16	252	292					0	-12	205	164
1	-11	275	278	0	-12	361	402	1	-14	464	511	0	-10	1214	1378
1	-10	343	355	0	-10	1258	1308	1	-13	190	221	0	-8	547	535
1	-9	321	352	0	-8	1244	127	1	-12	464	529	0	2	709	860
1	-8	196	125	0	2	1309	1417	1	-11	137	146	0	4	1017	1113
1	-7	1284	1223	0	4	719	680	1	-10	446	499	0	6	403	321
1	-6	1455	1365	0	6	90	110	1	-9	377	436	0	8	281	248
1	-5	472	479	0	8	979	926	1	-8	154	147	0	10	314	274
1	-4	2491	2561	0	10	432	417	1	-7	1099	1038	0	12	278	219
1	-3	2430	2473	0	12	177	197	1	-6	420	404	2	-16	190	240
1	1	803	842	0	14	260	237	1	-5	403	424	2	-15	182	177
1	2	411	354	2	-15	306	329	1	1	620	587	2	-13	409	373
1	3	334	310	2	-13	328	302	1	2	739	681	2	-12	112	112
1	4	927	950	2	-12	222	202	1	3	303	254	2	-11	585	643
1	5	158	115	2	-11	368	377	1	4	1049	974	2	-10	202	211
1	6	1008	1000	2	-10	378	325	1	5	439	411	2	-8	846	858
1	7	340	297	2	-9	136	123	1	6	961	916	2	-7	1046	1037
1	8	611	574	2	-8	1191	1267	1	8	307	390	2	-6	894	830
1	10	107	110	2	-7	1193	1248	1	10	380	328	2	-5	806	702

Table 3. (Continued)

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
2	1	140	119	2	10	420	376	4	2	119	113	6	-8	244	255
2	2	958	959	4	-15	197	239	4	3	546	530	6	-7	198	220
2	3	513	464	4	-13	536	514	4	4	249	265	6	-6	280	247
2	4	545	554	4	-11	362	343	4	5	698	728	6	-5	279	263
2	5	459	415	4	-8	417	392	4	7	596	539	6	2	526	417
2	7	521	445	4	-7	473	373	4	9	278	262	6	3	199	162
2	8	172	122	4	-5	1151	1105	6	-10	200	194	6	5	142	171
2	9	313	245	4	1	252	207								

Solution of the Structure of $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$

A red needle crystal with approximate dimensions 0.15 x 0.15 x 0.8 mm was mounted on a glass rod. This crystal was then mounted on the precession camera with the long dimension of the crystal, c axis, along the camera spindle axis. Viewed from the end the crystal appeared square. Orientation precession photographs were taken, using zirconium-filtered Mo Kα radiation $\lambda = 0.7106$Å. The symmetry of the precession photographs and the general absence of hkl reflections with $h + k + l = 2n + 1$ was consistent with the following space groups I422 (No. 97), I4mm (No. 107), $I\bar{4}m2$ (No. 119), $I\bar{4}2m$ (No. 121) and I4/mmm (No. 139). The space group ambiguity was resolved in favor of $I\bar{4}2m$ (No. 121) through the Patterson map and the successful refinement of the structure. The unit cell parameters measured from precession camera zero level Polaroid photographs are $a = b = 13.72(4)$Å, $c = 10.85(3)$Å, and V = 2042Å^3. The crystal was large and gave large spots on the film; it was difficult to measure these with a high degree of accuracy. When this crystal was obtained the only source of radiation available on the automated diffractometer was copper. As will be shown, this is a very poor choice for use with a crystal containing cobalt. The atomic absorption coefficient, μ_a of cobalt, for copper Kα ($\lambda = 1.5418$Å) radiation is 3240 cm^2 (51). The calculated linear absorption coefficient, μ, for $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$ using copper radiation is 133 cm^{-1}. Molydenum is the preferred radiation, with a linear absorption coefficient, μ, for $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$ using Kα radiation ($\lambda = 0.7107$Å) of

17 cm^{-1}. A unit cell volume of 2053.4$Å^3$ and two tetramers per unit cell were used in this calculation. A molydenum tube for the diffractometer was ordered, and the first set of data was collected with copper radiation. The same crystal used for the space group determination was transferred to the automated Picker four-circle diffractometer. The crystal was realigned on the diffractometer according to published instructions (52). The four angles (ϕ, χ, ω and 2θ) which define the position of the crystal and counter to record a reflection in reciprocal space, were determined for ten reflections. From these ten reflections, refined unit cell parameters and angle settings for the remaining data were obtained by a least-squares method using a computer program written by F. Carter and modified for the Univac 1108 computer by Bertrand and Kirkwood (53). The cell parameters obtained from this first alignment with Cu Kα radiation (λ = 0.7107) are $a = b$ = 13.77(3)Å, c = 10.83(2)Å and V = 2053.4$Å^3$.

It was not possible with this crystal to measure an experimental density. After one crystal was removed from the flask for X-ray work, all other crystals dissolved and repeated attempts could not produce more crystals. Although the original crystal was available it was considered more important to keep it for possible future X-ray work than to risk dissolving it in a density determination. The density calculated on the basis of two tetramers per unit cell (volume = 2053.4$Å^3$) is 1.44 g/cm^3.

The copper radiation intensities were collected by the θ-2θ scan technique with a takeoff angle of approximately 1.6° and a scan

rate of one degree per minute. A symmetrical scan of two degrees was taken about the calculated position for each reflection. When the scan was completed stationary background counts of one minute were taken at the beginning and at the end of the scan. All reflections in the positive octant (h, k and l all positive) were collected and equivalent reflections were averaged (h,k,l is equivalent to k,h,l). The intensity value was obtained by subtracting the backgrounds from the total integrated peak count. Two hundred and eighty-eight independent non-zero reflections were accepted as being statistically above background ($\sigma < 0.5$, where σ = (peak + background)$^{1/2}$ / (peak - background)). These reflections were corrected for Lorentz and polarization effects and were used to calculate the initial Patterson function.

Very early in the solution of the structure the molybdenum tube arrived. This was placed on the diffractometer and aligned. An entire new set of data was collected by the same method used to collect the data with copper radiation. The four angles which define the position of the crystal and counter to record a reflection in reciprocal space were determined for four reflections. From these four reflections, refined unit cell parameters and angle settings for the remaining data were obtained by a least-squares method using the Carter program (53). The cell parameters obtained from the diffractometer data are $a = b =$ 13.87(3)Å, c = 10.81(2)Å and V = 2080.4Å^3, using Mo radiation, λ = 0.7107Å. The molybdenum intensity data was collected by the θ-2θ scan technique with a takeoff angle of 1.6° and a scan rate of one degree per minute. A symmetrical scan of two degrees was taken about the

calculated position for each reflection. When the scan was completed stationary backgrounds were collected for one minute at the beginning and at the end of the scan. All reflections in the positive octant (h, k and l all positive) were collected and equivalent reflections were averaged (h,k,l is equivalent to k,h,l). The intensity value was obtained by subtracting the backgrounds from the total integrated peak count. Data were collected for 1863 calculated positions in the positive octant. The limits set in the Carter program were h from zero to 24, k from zero to 11 and l from zero to 14. This essentially collected all possible data within the Ewald sphere. Three hundred and twenty-one nonzero unique reflections were accepted as being statistically above background ($\sigma < 0.5$, where σ = (peak + background)$^{1/2}$ / (peak - background)) and were used in the refinement. The intensities were corrected for Lorentz and polarization effects but were not corrected for absorption (μ = 17 cm^{-1}). For the $00l$ reflections, rotation around ϕ did not cause more than 5 per cent variation in intensity. Periodic checks of standard reflections showed no significant variation. Computations were carried out as described earlier.

A three-dimensional Patterson function was calculated using the 288 unique nonzero reflections from the copper data. The distribution of peaks on the Patterson map was consistent with the noncentrosymmetric space group, $1\bar{4}2m$ (No. 121). From this Patterson function positions were obtained for the cobalt (Co7) and the three oxygens (O1, O8 and O9). The cobalt atom and two oxygen atoms, O8 and O9, were placed in

the Wyckoff 8i set on the mirror plane. The other oxygen atom, O1, was placed in a general position, Wyckoff 16j set. A subsequent electron density calculation based on these atoms revealed the position of the methoxide carbon, C10. It was placed in the Wyckoff 8i set on the mirror plane. The structure was quite confusing at this point due to a disorder problem. After much trial and error following a false start in which the molecule was assumed to have $\bar{4}2m$ symmetry, the carbon atoms of the actylacetonate group (C2, C3, C4, C5 and C6) were placed in the structure factor calculations with multipliers of 0.5 in order to place half of the electron density in each of the disordered positions. This disorder could result from one isomeric form positioned in different orientations throughout the lattice, or a mixture of different geometric isomers could also lead to the same result. It is not possible at this point to say which is the case. There does not appear to be a methanol group present in this molecule as in $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$. No appreciable electron density occurs at the expected point in a final difference electron density map calculation. Also if a carbon atom is placed at the calculated position and allowed to refine in a least-squares technique the isotropic temperature factor rises to a very unreasonable value. After several cycles of least-squares refinement of the scale factor, atomic coordinates and isotropic temperature factors the structure converged to a conventional R_1 value ($\Sigma||Fo| - |Fc|| \,/\, \Sigma|Fo|$) of 0.095. With all reflections weighted at unity, the value of R_2 ($\{\Sigma_i w_i (|Fo| - |Fc|)^2 \,/\, \Sigma_i w_i (|Fo|)^2\}^{1/2}$) was 0.092.

In the structure factor calculations, the scattering factors tabulated by Ibers (51) were employed for all atoms. The positional and thermal parameters derived from the last cycle of the least-squares refinement are presented in Table 4. The observed and calculated structure factors (molybdenum data) for the 221 nonzero unique reflections are given in Table 5.

Table 4. Final Positional and Thermal Parameters for $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$

Atom	x	y	z	B, A^2
O1	0.2378(13)	0.0752(15)	0.0824(18)	9.4(5)
C2	0.3916(50)	0.0761(54)	0.1350(58)	12.0(19)
C3	0.3068(29)	0.0966(31)	0.1731(33)	4.4(8)
C4	0.2731(46)	0.1125(47)	0.2907(56)	10.3(17)
C5	0.1824(34)	0.1172(29)	0.3356(44)	5.7(11)
C6	0.1608(89)	0.1383(86)	0.4735(59)	12.5(26)
Co7	0.0820(4)	0.0820(4)	0.0980(4)	5.2(1)
O8	0.0666(19)	0.0666(19)	-0.08731(17)	5.0(4)
O9	0.0965(15)	0.0965(15)	0.2848(20)	6.8(5)
C10	0.1288(37)	0.1288(37)	-0.1705(32)	6.7(9)

Table 5. Observed and Calculated Structure Factors for $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$

H	K	FO	FC
	L= 0		
4	0	180	186
6	0	227	237
8	0	49	57
10	0	38	37
12	0	45	48
3	1	24	29
5	1	141	146
7	1	93	100
11	1	29	33
13	1	34	32
4	2	20	14
6	2	70	70
8	2	26	30
12	2	25	22
4	4	55	53
6	4	48	43
8	4	14	10
10	4	13	16
12	4	12	14
5	5	110	106
7	5	79	70
11	5	27	33
13	5	26	24
6	6	141	133
8	6	55	53
10	6	21	21
12	6	36	37
14	6	13	13
7	7	86	81
11	7	24	23
13	7	27	23
8	8	19	16
12	8	20	15
	L= 1		
5	0	115	129
7	0	116	132
11	0	22	28
13	0	35	35
4	1	83	86
6	1	122	125
8	1	49	58
10	1	20	23
12	1	32	30
14	1	13	18
5	2	54	53
7	2	47	49
9	2	42	47
11	2	12	12
13	2	19	20
4	3	68	60
6	3	10	6
8	3	37	43
10	3	26	30
14	3	14	16
5	4	46	42
7	4	48	46
9	4	36	36
13	4	16	17
6	5	82	75
8	5	38	29
12	5	22	21
14	5	14	10
7	6	81	71
9	6	13	16
11	6	19	20
13	6	24	23
8	7	37	37
10	7	20	18
12	7	27	23
9	8	27	26
11	8	17	13
13	8	13	10
	L= 2		
4	0	25	26
6	0	34	35
8	0	24	31
10	0	12	14
12	0	20	17
1	1	61	58
3	1	69	66
5	1	68	73
7	1	45	46
9	1	37	44
11	1	15	18
13	1	13	15
4	2	68	67
6	2	35	32
8	2	44	48
10	2	29	32
12	2	13	9
14	2	15	20
3	3	46	43
5	3	54	49
7	3	46	45
9	3	46	44
11	3	15	15
13	3	15	14
4	4	59	49
6	4	9	11
9	5	24	22
13	5	14	9
6	6	45	36
8	6	18	14
12	6	15	10
7	7	31	25
9	7	25	22
11	7	13	12
8	8	35	28
10	8	23	19
9	9	31	28
11	9	12	9
10	10	12	15
	L= 3		
5	0	31	33
7	0	11	10
2	1	74	70
4	1	47	52
6	1	19	17
8	1	32	31
10	1	16	23
3	2	61	54
5	2	40	37
7	2	31	36
9	2	33	34
11	2	18	18
13	2	12	11
4	3	26	25
6	3	19	17
8	3	48	46
10	3	19	26
14	3	13	17
5	4	44	41
7	4	37	35
9	4	29	31
11	4	14	15
13	4	13	12
6	5	13	13
8	5	32	29
10	5	13	17
7	6	23	17
8	7	24	22
10	7	17	17
12	7	13	7
9	8	28	26
11	8	16	15
10	9	17	18
	L= 4		
0	0	178	168
2	0	71	64
4	0	34	38
6	0	81	92
8	0	43	41
10	0	11	12
12	0	24	26
1	1	97	99
3	1	65	59
5	1	48	51
7	1	63	63
9	1	14	17
11	1	12	17
13	1	20	18
2	2	116	108
4	2	46	44
6	2	37	37
8	2	46	47
10	2	11	17
12	2	13	15
3	3	32	29
5	3	24	21
7	3	44	43
9	3	16	22
11	3	11	7
4	4	15	20
6	4	17	20
8	4	31	30
10	4	11	16
5	5	36	36
7	5	48	40
9	5	16	16
11	5	12	15
13	5	15	15
6	6	60	54
8	6	37	30
12	6	21	20
7	7	48	41
9	7	19	16
11	7	18	14
8	8	28	24
10	8	17	16
9	9	18	13
	L= 5		
1	0	186	172
3	0	9	4
5	0	91	99
7	0	92	94
11	0	28	35
13	0	28	23
2	1	58	56
4	1	38	39
6	1	96	102
8	1	32	34
10	1	13	14
12	1	29	31
3	2	12	15

Table 5. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
5	2	33	35	2	2	54	51	9	2	19	21	4	1	12	17
7	2	43	44	4	2	40	37	4	3	35	37	6	1	14	20
11	2	13	15	6	2	42	38	8	3	28	32	8	1	13	14
13	2	12	12	8	2	19	23	10	3	13	17	3	2	10	15
4	3	9	9	10	2	14	16	5	4	13	17	5	2	15	16
6	3	10	13	12	2	14	11	7	4	16	19	7	2	13	15
5	4	23	26	3	3	66	57	9	4	16	18	7	4	13	15
7	4	32	29	5	3	20	20	6	5	11	10	6	5	11	12
11	4	12	17	7	3	21	22	8	5	13	18	7	6	14	16
6	5	67	67	9	3	24	24	7	6	19	19				
8	5	27	24	4	4	36	30	9	8	14	14		L=10		
10	5	12	11	6	4	31	27								
12	5	23	23	8	4	23	21		L= 8			0	0	38	41
7	6	70	63	10	4	12	13					2	0	19	21
11	6	22	25	5	5	39	34	2	0	13	8	6	0	27	31
13	6	18	17	7	5	42	38	1	1	20	17	8	0	12	12
8	7	25	23	11	5	13	13	3	1	23	21	1	1	29	31
10	7	12	8	6	6	67	60	2	2	52	44	5	1	19	24
12	7	19	18	8	6	18	17	4	2	19	21	7	1	17	21
				12	6	20	17	8	2	18	20	6	2	13	14
	L= 6			7	7	37	36	10	2	13	14	6	4	12	12
				11	7	13	13	3	3	31	28	5	5	15	19
0	0	99	96					5	3	12	12	7	5	13	15
2	0	62	58		L= 7			7	3	13	15	6	6	20	21
4	0	10	6					9	3	19	18	7	7	13	14
6	0	91	89	1	0	33	35	4	4	16	17				
8	0	29	36	5	0	11	10	8	4	16	17		L=11		
12	0	32	27	7	0	21	28	10	4	13	15				
1	1	96	85	2	1	22	26	5	5	14	13	1	0	28	28
3	1	39	37	4	1	22	22					5	0	23	22
5	1	53	51	6	1	20	22		L= 9			7	0	15	15
7	1	63	63	8	1	14	20					2	1	11	12
9	1	12	13	3	2	52	52	1	0	17	23	6	1	16	16
11	1	17	20	5	2	20	23	7	0	17	22	3	2	12	13
13	1	19	16	7	2	22	29	2	1	16	21	6	5	14	14

Solution of the Structure of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ (18)

The data collection for this compound was performed by Kaplan. The structure was partially solved by Bertrand. The final structure refinement was carried out by Bertrand and Kirkwood. A needle-like crystal of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ with approximate dimensions 0.10 x 0.20 x 0.80 mm was sealed inside a Lindemann glass capillary. The crystal was mounted on a precession camera with the long dimension (a) of the crystal parallel to the spindle axis. The shortest dimension of the crystal corresponds to the b axis. The unit cell dimensions, obtained at room temperature from zero-level precession photographs using zirconuim-filtered Mo Kα radiation (λ = 0.7107Å), are a = 21.79(4)Å, b = 10.88(2)Å, c = 20.00(4)Å, β = 121.4(1)° and V = 4086Å^3. The calculated density of 1.43 g/cm^3, based on four tetramers per unit cell, agrees well with the experimental value of 1.40(3) g/cm^3 obtained by the flotation method using a mixture of carbon tetrachloride and hexane.

From zero and upper level precession photographs, the systematic absences were noted; the absence of hkl reflections with $h + k = 2n + 1$ and the absence of $h0l$ reflections with $l = 2n + 1$ indicated space group Cc (No. 9) or C2/c (No. 15). The space group ambiguity was resolved in favor of C2/c through the Patterson map and the successful refinement of the structure.

Intensity data were collected on the precession camera with zirconium-filtered Mo Kα radiation, using the same crystal used for the space group determination. A total of 1557 nonzero unique reflections

from the $hk\ell$(ℓ = 0 to -3) and $hk\ell$(k = 0 to 3) levels were visually estimated from exposures of 0.5, 5.0 and 50 hours. Lorentz-polarization corrections were computed. No corrections for absorption were made (μ = 13 cm^{-1}); the maximum error in F was estimated as 5 per cent. Computations were carried out as described earlier.

A three-dimensional Patterson function was computed. Due to the superposition of cobalt-to-oxygen vectors, the cobalt-to-cobalt vectors were not easily chosen. However, since the tetramer was required to occupy a site of twofold symmetry and since a cubane type structure was expected, it was possible to assign, from the Patterson function, coordinates for the cobalt and oxygens of the cubane portion of the structure. Successive cycles of structure factor and electron density calculations were used to obtain coordinates for the remaining nonhydrogen atoms. Full-matrix least-squares refinement (each reflection assigned unit weight) of individual layer scale factors, individual isotropic temperature factors and atomic coordinates for the 24 atoms of the asymetric unit (80 parameters) converged to a conventional R_1 value ($\Sigma||Fo| - |Fc|| / \Sigma|Fo|$) of 0.10. The atomic positional parameters and isotropic temperature factors derived from the last cycle of refinement are presented in Table 6. The final observed and calculated structure factors are given in Table 7.

Table 6. Final Positional and Thermal Parameters for $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$

Atom	x	y	z	B, A^2
Co1	0.0852(1)	0.0237(3)	0.2992(2)	3.08(6)
Co2	0.0023(1)	0.2219(3)	0.1729(2)	3.04(6)
O1	-0.0008(5)	0.0299(12)	0.1822(7)	2.53(23)
O2	0.0733(6)	0.2118(12)	0.2897(7)	2.65(24)
O3	0.1586(8)	0.0489(17)	0.4219(9)	5.44(37)
O4	0.0962(7)	0.2046(17)	0.1600(8)	4.30(32)
R1O1*	0.1628(6)	0.0281(14)	0.2708(7)	3.48(27)
R1O2	0.0985(7)	-0.1581(15)	0.3152(9)	4.27(33)
R2O1	0.0065(7)	0.4038(15)	0.1618(9)	4.41(35)
R2O2	-0.0747(7)	0.2095(15)	0.0569(8)	4.15(31)
C1	0.0015(9)	-0.0494(24)	0.1284(12)	4.11(45)
C2	0.1343(9)	0.2958(20)	0.3268(12)	3.45(38)
C3	-0.2170(19)	-0.0138(37)	0.0200(23)	9.03(92)
C4	0.0952(12)	0.1874(29)	0.0864(14)	5.46(57)
R1C1	0.2040(11)	-0.0624(23)	0.2760(13)	4.35(46)
R1C2	0.1471(10)	-0.2251(24)	0.3139(12)	4.30(44)
R1C3	0.2601(12)	-0.0382(27)	0.2557(15)	5.34(52)
R1C4	0.1985(11)	-0.1821(25)	0.2953(14)	4.85(50)
R1C5	0.1472(14)	-0.3613(29)	0.3343(17)	6.52(69)
R2C1	-0.0237(11)	0.4658(26)	0.1002(14)	4.46(45)
R2C2	-0.0969(11)	0.3010(23)	0.0087(14)	4.42(46)

Table 6. (Continued)

Atom	x	y	z	B, A^2
R2C3	-0.0023(13)	0.6044(30)	0.1100(17)	6.30(68)
R2C4	-0.0746	0.4194(26)	0.0241(15)	5.47(56)
R2C5	-0.1550(14)	0.2639(31)	-0.0754(17)	7.45(73)

*R1 and R2 refer to the chelate rings.

Table 7. Observed and Calculated Structure Factors for $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$

H	K	FO	FC
	L= 0		
0	4	351	394
0	10	23	30
0	12	60	52
1	3	48	38
1	5	413	368
1	7	74	75
1	9	69	70
1	11	80	70
1	13	12	9
2	2	112	114
2	4	148	145
2	6	50	47
2	8	23	19
2	10	28	34
2	12	32	31
3	3	115	119
3	5	130	132
3	7	65	78
3	9	66	70
3	11	59	53
3	13	21	20
4	2	60	53
4	4	29	18
4	6	131	124
5	1	59	73
5	3	27	29
5	5	25	17
5	7	111	111
5	9	25	19
5	11	45	43
5	13	24	23
6	0	76	69
6	2	87	73
6	4	12	3
6	6	138	145
7	1	105	110
7	7	94	79
7	9	19	18
7	11	51	46
7	13	26	24
8	0	146	151
8	2	98	101
8	4	26	34
8	6	65	67
8	8	22	13
9	3	50	51
9	5	91	92
9	7	38	41
9	9	31	31
9	11	52	36
9	13	23	19
10	0	275	287
10	2	44	41
10	4	85	88
11	1	143	166
11	5	181	186
11	7	39	32
11	9	37	43
11	11	62	42
12	0	364	343
12	2	23	23
12	4	146	157
12	12	30	30
13	1	119	107
13	3	41	47
13	5	152	150
13	7	37	43
13	9	51	51
13	11	50	44
14	0	173	188
14	2	45	42
14	4	102	87
14	6	33	39
14	8	26	9
14	12	17	21
15	3	32	23
15	5	62	56
15	7	44	55
15	9	34	28
15	11	27	31
16	2	82	79
16	6	56	52
17	1	41	43
17	3	53	49
17	7	37	44
17	9	28	18
17	11	36	21
18	2	58	56
18	6	41	41
19	3	29	28
19	7	28	34
20	0	53	50
20	2	41	44
21	5	22	26
21	7	25	12
22	0	57	53
22	4	27	32
23	1	38	36
23	3	28	22
23	5	34	32
24	0	55	53
24	4	26	35
	L=-1		
-23	1	29	39
-23	5	29	28
-22	2	16	16
-22	6	33	36
-21	1	20	32
-21	3	16	16
-21	5	30	25
-20	6	19	17
-19	1	16	18
-19	3	28	38
-19	7	25	23
-19	9	18	3
-18	4	23	27
-18	6	16	11
-18	8	39	31
-17	1	27	41
-17	3	39	46
-17	7	34	41
-17	9	19	15
-16	4	48	48
-16	6	16	4
-16	8	50	53
-16	10	16	5
-15	1	51	58
-15	3	78	78
-15	7	39	44
-15	9	20	17
-14	2	18	32
-14	4	65	60
-14	6	35	53
-14	8	32	27
-14	10	43	38
-13	1	114	126
-13	3	42	39
-13	5	72	73
-13	9	16	11
-13	11	34	35
-12	2	91	103
-12	4	36	43
-12	6	160	165
-12	10	78	73
-11	1	179	175
-11	3	29	41
-11	5	152	134
-11	7	26	31
-11	9	50	35
-11	11	55	52
-10	2	32	25
-10	4	35	46
-10	6	152	157
-10	8	24	21
-10	10	89	91
-9	1	119	128
-9	3	65	90
-9	5	68	76
-9	7	23	30
-9	9	15	7
-9	11	33	33
-8	2	43	49
-8	4	62	57
-8	6	33	28
-8	8	53	50
-8	10	39	38
-8	12	31	27
-7	1	61	56
-7	3	45	58
-7	5	20	17
-7	7	46	52
-7	9	30	33
-6	2	10	7
-6	6	25	25
-6	8	38	31
-6	12	57	52
-5	1	23	23
-5	3	81	77
-5	7	103	93
-5	9	23	11
-5	11	36	31
-5	13	26	23
-4	2	9	2
-4	4	154	157
-4	8	116	100
-4	12	62	52
-3	1	170	186
-3	3	143	150
-3	7	64	75
-3	13	26	17
-2	2	150	155
-2	4	188	187
-24	2	15	16
-2	6	185	183
-2	8	85	76
-2	10	74	61
-1	3	100	90
-1	5	166	165
-1	7	53	60
-1	9	40	36
-1	11	78	76
-1	13	20	3
0	2	81	68
0	4	34	42
0	6	189	222
0	10	139	140
0	14	33	34
1	3	104	79
1	5	310	306
1	7	83	90
1	9	57	49

Table 7. (Continued)

H	K	FO	FC
1	11	287	101
2	2	65	66
2	6	182	199
2	8	16	10
2	10	107	110
2	14	28	26
3	3	108	105
3	5	143	140
3	11	27	31
4	2	94	91
4	4	213	206
4	6	29	27
4	8	106	104
4	10	48	44
4	12	43	40
5	1	27	49
5	3	21	74
5	7	87	86
5	11	22	17
5	13	26	20
6	2	15	14
6	4	116	118
6	6	19	10
6	8	63	74
6	12	62	53
7	1	87	81
7	3	54	42
7	5	19	19
7	7	47	37
7	9	45	31
7	11	32	28
7	13	26	24
8	2	53	55
8	4	66	85
8	8	61	63
8	12	40	37
9	1	99	95
9	3	87	106
9	5	39	43
9	7	14	26
9	11	16	9
10	4	41	46
10	6	70	68
10	8	50	48
10	10	64	52
11	1	77	77
11	3	48	48
11	5	109	92
11	7	14	20
11	9	54	46
11	11	43	45
12	2	63	60
12	4	24	16
12	6	115	131
12	10	81	72
13	1	110	102
13	5	120	120
13	7	51	62
13	9	48	43
13	11	46	47
14	2	41	43
14	6	72	69
14	10	54	54
15	1	67	76
15	3	70	60
15	5	31	35
15	7	16	10
16	4	63	61
16	8	46	43
16	12	25	21
17	1	61	65
17	3	55	54
17	5	19	3
17	7	32	31
17	9	16	20
18	2	16	17
18	4	39	61
18	6	16	16
18	8	56	47
19	1	20	22
19	3	40	39
19	7	30	26
20	4	23	28
20	8	25	24
21	3	16	19
21	5	16	15
22	6	15	16
23	1	16	21
23	5	22	21
24	6	24	24

L=-2

H	K	FO	FC
-24	0	35	40
-23	1	29	28
-23	5	22	30
-22	0	48	51
-22	4	27	35
-21	5	24	30
-20	0	42	49
-20	4	19	22
-19	5	19	19
-19	7	24	15
-18	2	24	35
-18	6	24	24
-17	1	32	38
-17	3	30	39
-17	7	19	25
-16	2	66	70
-16	4	19	13
-16	6	39	38
-16	8	19	7
-15	1	29	32
-15	3	37	44
-15	7	39	39
-15	9	19	8
-14	0	44	49
-14	2	86	92
-14	4	22	27
-14	6	30	30
-14	10	28	15
-13	1	29	33
-13	5	77	71
-13	7	29	38
-13	9	51	36
-13	11	24	22
-12	0	157	174
-12	4	118	108
-12	8	26	23
-12	10	19	13
-11	1	169	164
-11	3	42	51
-11	5	155	150
-11	7	28	29
-11	9	50	42
-11	11	34	32
-10	0	199	204
-10	2	31	35
-10	4	97	95
-9	1	92	100
-9	3	19	11
-9	5	89	102
-9	7	17	12
-9	9	18	25
-9	11	39	26
-8	0	109	106
-8	2	50	45
-8	4	35	46
-8	6	34	27
-7	1	61	50
-7	5	33	29
-7	7	20	3
-7	9	31	30
-7	11	38	33
-6	0	34	39
-6	2	145	155
-6	4	27	30
-6	6	73	71
-5	1	101	101
-5	3	55	57
-5	5	31	22
-5	7	85	86
-5	11	30	28
-4	0	9	9
-4	2	165	153
-4	4	37	41
-4	6	120	108
-4	8	38	44
-3	1	24	49
-3	3	93	87
-3	7	72	76
-3	9	26	22
-3	11	23	20
-2	2	135	139
-2	4	61	58
-2	6	49	48
-2	8	24	31
-2	10	28	16
-1	3	29	27
-1	5	153	140
-1	7	30	36
-1	9	52	51
-1	11	34	26
0	2	56	63
0	4	182	184
0	6	56	58
0	8	26	28
0	12	36	25
1	3	165	142
1	5	212	224
1	7	28	22
1	9	38	46
1	11	47	41
2	2	88	93
2	4	178	182
2	6	45	51
2	8	50	47
2	12	30	23
3	3	83	83
3	5	76	88
3	9	51	46
3	11	43	36
4	2	40	53
4	4	86	76
4	6	58	58
5	1	112	105
5	3	149	130
5	5	12	18
5	7	53	56
5	9	31	26
5	11	22	18
6	0	49	54
6	2	157	161
6	6	87	75
6	8	25	29
6	10	18	17

Table 7. (Continued)

H	K	FO	FC
7	1	120	128
7	3	94	92
7	7	85	83
7	9	42	30
8	0	56	57
8	2	131	123
8	6	75	71
8	8	16	23
9	1	88	85
9	3	84	94
9	5	27	15
9	7	60	58
9	11	19	12
10	0	63	66
10	2	24	31
11	1	105	106
11	5	60	56
11	11	19	8
12	0	110	110
12	2	122	122
12	4	103	106
12	6	56	53
12	8	31	46
13	1	109	108
13	3	78	77
13	5	73	69
13	9	33	36
14	0	131	127
14	2	53	57
14	4	87	87
14	6	18	22
14	8	18	20
15	1	60	52
15	3	37	31
15	5	36	33
15	7	18	24
15	9	23	16
16	0	65	68
16	2	44	48
16	4	43	38
17	1	55	47
17	3	41	47
17	7	23	21
17	9	28	15
18	0	26	24
18	2	76	65
18	6	33	28
19	1	33	28
19	3	53	52
19	7	27	30
20	2	27	29
20	4	19	15
20	6	24	19
21	3	31	25
23	1	20	20
23	3	28	25
24	0	31	29
24	2	29	27
24	4	24	26
25	1	27	30
25	3	30	27
26	0	19	19
L=-3			
-16	4	37	44
-17	7	16	20
-16	8	33	38
-16	10	16	15
-15	1	25	31
-15	3	28	34
-15	5	22	22
-15	7	32	36
-15	9	30	28
-14	4	31	34
-14	8	26	22
-13	1	52	63
-13	3	27	23
-12	2	20	35
-12	6	33	42
-12	8	18	22
-12	10	27	22
-11	1	29	37
-11	3	16	22
-11	5	53	57
-11	7	32	39
-11	9	36	33
-11	11	33	31
-10	2	34	28
-10	4	39	49
-10	6	83	93
-10	8	35	30
-10	10	62	55
-9	1	14	9
-9	3	49	48
-9	5	77	72
-9	7	20	12
-9	9	50	52
-9	11	30	26
-8	4	23	26
-8	6	62	66
-8	8	16	5
-8	10	31	29
-7	1	31	34
-7	5	20	21
-7	7	15	19
-6	2	29	19
-6	4	24	23
-5	1	45	40
-5	3	50	49
-5	5	40	50
-5	7	51	52
-5	9	58	59
-5	11	25	25
-4	2	20	25
-4	4	116	113
-4	6	45	49
-4	8	45	47
-4	10	34	34
-4	12	37	39
-3	1	128	140
-3	5	67	75
-3	7	65	55
-3	9	65	72
-3	11	43	41
-2	2	58	63
-2	4	67	59
-2	6	54	62
-2	8	25	28
-2	12	18	25
0	4	109	99
0	6	70	54
0	8	59	55
0	10	66	57
0	12	18	22
1	3	75	64
1	5	122	127
1	7	46	48
1	9	79	82
1	11	69	57
2	4	239	236
2	6	133	123
2	8	111	92
2	10	70	66
2	12	31	31
3	3	114	104
3	5	116	95
3	7	47	61
3	9	36	40
3	11	30	30
4	4	17	13
4	6	78	87
4	10	20	16
5	3	28	39
5	5	28	23
5	7	21	16
6	2	13	7
6	4	57	72
6	8	23	26
6	12	18	17
7	1	129	116
7	3	53	66
7	5	62	75
7	7	45	35
7	9	51	59
7	11	49	36
8	4	78	83
8	6	75	76
8	8	31	34
8	10	73	59
8	12	35	32
9	1	21	22
9	5	42	38
9	7	24	17
9	9	65	57
9	11	25	25
10	2	45	42
10	6	23	26
11	1	51	49
11	3	46	44
11	5	42	39
11	7	16	2
11	9	27	30
12	2	14	10
12	4	72	68
12	6	55	51
12	8	34	30
12	10	29	28
12	12	23	23
13	1	25	23
13	3	75	77
13	5	75	78
13	7	60	59
13	9	69	65
13	11	30	27
14	2	37	38
14	4	51	58
14	6	48	53
14	8	43	48
14	10	23	28
14	12	27	28
15	1	16	15
15	3	16	25
15	5	21	22
15	7	30	43
15	9	29	27
15	11	19	21
17	1	21	32
18	2	18	8
18	4	18	18
18	6	18	16
18	8	19	18
18	10	19	20
19	3	18	22
19	5	29	27
19	7	23	18

Table 7. (Continued)

H	K	FO	FC
20	2	18	18
20	4	19	20
20	6	27	30
20	8	23	21
20	10	19	18
21	1	23	29
21	3	13	10
23	3	19	20

H	L	FO	FC
	K=	0	
-28	10	27	26
-28	12	27	27
-28	14	15	9
-28	16	18	22
-28	18	41	50
-28	20	27	35
-26	14	11	10
-26	16	20	26
-26	18	32	32
-26	20	19	17
-24	6	40	40
-24	8	55	44
-24	10	23	19
-24	12	26	15
-24	14	11	3
-24	22	23	25
-24	24	30	28
-22	4	63	52
-22	6	107	116
-22	8	79	73
-22	10	20	19
-22	12	31	35
-22	14	53	61
-22	16	41	42
-22	18	20	6
-22	22	20	5
-20	4	103	106
-20	6	121	122
-20	8	26	34
-20	10	52	49
-20	12	152	150
-20	14	117	120
-20	16	53	51
-20	20	42	44
-20	22	36	33
-18	4	97	105
-18	6	72	71
-18	8	11	18
-18	10	100	98
-18	12	147	146
-18	14	75	77
-18	18	103	99

H	L	FO	FC
-18	20	108	105
-18	22	49	50
-16	8	56	50
-16	10	96	103
-16	12	30	32
-16	14	19	30
-16	16	43	44
-16	18	123	121
-16	20	83	87
-16	24	27	36
-16	26	44	56
-14	6	29	36
-14	8	49	55
-14	12	42	36
-14	14	36	24
-14	16	49	55
-14	18	56	67
-14	20	44	39
-14	22	32	38
-14	24	40	50
-14	26	38	47
-12	4	32	49
-12	6	165	155
-12	8	136	131
-12	22	38	44
-12	24	30	36
-12	26	19	17
-10	4	194	191
-10	6	490	491
-10	8	230	230
-10	10	145	131
-10	12	36	25
-10	14	135	146
-10	16	62	79
-10	24	17	5
-8	4	368	371
-8	6	466	480
-8	8	72	74
-8	10	25	30
-8	12	321	309
-8	14	317	303
-8	16	118	120
-8	18	42	35
-8	20	48	55
-8	22	46	47
-6	4	447	412
-6	6	76	56
-6	8	75	67
-6	10	196	212
-6	12	261	250
-6	14	146	140
-6	18	103	121
-6	20	114	120
-6	22	44	50

H	L	FO	FC
-4	4	117	122
-4	6	64	57
-4	8	145	140
-4	10	119	115
-4	12	26	19
-4	14	10	4
-4	16	64	67
-4	18	82	97
-4	20	68	66
-4	24	11	21
-2	4	25	35
-2	6	25	66
-2	8	91	89
-2	10	15	35
-2	12	13	21
-2	16	30	30
-2	18	41	39
-2	20	21	24
-2	24	20	26
0	6	250	268
0	8	333	319
0	10	144	130
0	12	67	56
0	14	51	45
2	4	485	460
2	6	560	558
2	8	221	270
2	10	56	72
2	12	95	89
2	14	124	120
2	16	50	53
4	4	135	150
4	6	237	214
4	8	30	16
4	10	47	44
4	12	108	121
4	14	138	144
4	16	31	44
4	20	19	26
6	4	128	124
6	6	62	72
6	8	39	36
6	10	31	42
6	12	100	99
6	14	58	69
6	18	25	30
8	4	29	37
8	8	19	4
8	10	51	53
8	12	58	58
8	14	26	19
8	16	23	19
8	18	27	34
10	4	46	33

H	L	FO	FC
10	6	41	37
10	8	28	44
10	10	26	25
10	16	10	12
12	6	65	74
12	8	99	108
12	10	43	49
12	14	19	20
14	4	33	48
14	6	113	117
14	8	92	87
14	12	15	22
16	4	63	63
16	6	84	77
16	8	37	33
20	4	16	17
24	0	54	53

H	L	FO	FC
	K=	1	
-29	18	27	26
-29	19	24	29
-29	20	23	28
-27	8	17	17
-27	19	17	19
-25	5	17	18
-25	7	35	36
-25	10	17	21
-25	12	35	29
-25	14	35	23
-25	19	17	15
-23	5	39	41
-23	6	35	29
-23	7	55	58
-23	8	49	47
-23	10	49	44
-23	11	38	35
-23	12	38	32
-23	13	38	46
-23	16	27	21
-23	18	30	29
-23	19	24	28
-23	20	35	26
-21	4	49	48
-21	5	69	74
-21	6	59	61
-21	7	45	48
-21	8	48	50
-21	10	20	29
-21	11	58	65
-21	12	23	26
-21	13	74	82
-21	14	70	74
-21	16	62	56

Table 7. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
-21	17	37	28	-15	26	31	35	-7	7	107	106	-1	13	91	80
-21	18	45	42	-13	4	88	97	-7	8	55	51	-1	14	48	46
-21	19	29	34	-13	5	38	45	-7	9	60	55	-1	17	25	33
-21	25	21	23	-13	6	57	59	-7	10	105	112	-1	18	16	24
-19	4	53	46	-13	7	112	121	-7	11	78	83	-1	19	41	43
-19	5	44	51	-13	8	76	76	-7	12	168	166	1	5	40	45
-19	6	28	29	-13	10	103	112	-7	13	151	155	1	6	191	206
-19	7	23	21	-13	11	60	64	-7	14	119	121	1	7	228	214
-19	10	39	31	-13	12	70	66	-7	15	68	67	1	8	244	263
-19	11	57	67	-13	13	36	34	-7	16	45	54	1	9	55	57
-19	12	96	92	-13	14	74	65	-7	17	42	36	1	10	106	120
-19	13	76	72	-13	17	37	48	-7	19	48	45	1	11	57	52
-19	14	90	87	-13	18	22	25	-7	20	57	61	1	12	55	62
-19	16	36	37	-13	19	45	49	-7	21	48	38	1	13	62	59
-19	17	43	37	-13	20	23	20	-7	22	46	50	1	15	35	20
-19	19	44	42	-13	24	30	30	-5	4	228	207	1	16	56	56
-19	20	59	51	-13	25	25	35	-5	5	101	107	1	17	33	27
-19	21	24	22	-11	5	157	132	-5	6	32	41	1	18	24	34
-19	22	49	48	-11	6	95	93	-5	7	125	115	1	19	30	31
-19	24	25	29	-11	7	218	250	-5	8	75	71	3	4	242	208
-17	5	47	45	-11	8	231	242	-5	10	85	89	3	5	169	177
-17	7	64	61	-11	9	38	29	-5	11	119	124	3	6	214	229
-17	8	48	41	-11	10	92	91	-5	12	27	37	3	7	230	235
-17	9	43	39	-11	11	72	68	-5	13	88	95	3	8	107	106
-17	10	66	52	-11	12	61	63	-5	15	56	50	3	9	108	112
-17	11	52	63	-11	13	95	78	-5	17	34	28	3	10	28	30
-17	12	57	57	-11	15	29	18	-5	18	50	58	3	11	25	16
-17	13	57	55	-11	16	59	64	-5	19	65	60	3	12	23	38
-17	15	38	34	-11	17	25	22	-5	20	67	72	3	13	71	69
-17	16	22	19	-11	18	48	52	-5	21	38	34	3	14	89	96
-17	17	39	30	-11	19	31	33	-5	22	30	31	3	15	57	53
-17	18	64	68	-11	20	16	20	-3	4	151	150	3	16	60	67
-17	19	63	60	-11	25	22	26	-3	5	22	41	3	19	24	14
-17	20	69	64	-9	4	205	186	-3	7	141	137	5	4	69	78
-17	21	38	35	-9	5	245	232	-3	8	70	64	5	5	193	180
-17	22	34	32	-9	6	299	278	-3	9	30	17	5	6	40	48
-17	26	22	25	-9	7	169	172	-3	10	22	15	5	7	94	116
-15	4	80	78	-9	8	185	170	-3	11	108	114	5	8	62	70
-15	5	61	67	-9	9	31	39	-3	12	51	44	5	9	38	34
-15	6	88	92	-9	10	54	43	-3	13	73	71	5	10	55	69
-15	7	77	79	-9	11	107	100	-3	14	70	73	5	11	43	48
-15	8	77	68	-9	12	52	49	-3	17	19	28	5	12	59	60
-15	11	75	85	-9	13	172	167	-3	18	28	29	5	13	86	90
-15	12	20	24	-9	14	133	136	-3	19	58	55	5	14	44	49
-15	13	54	60	-9	15	50	55	-3	21	30	26	5	15	51	51
-15	14	50	46	-9	16	76	86	-1	4	163	177	5	20	24	28
-15	15	25	18	-9	17	39	32	-1	5	140	131	5	21	23	22
-15	16	48	43	-9	18	53	61	-1	6	156	132	7	4	31	43
-15	17	41	46	-9	19	42	37	-1	7	200	179	7	5	71	74
-15	18	38	38	-9	21	29	28	-1	8	53	48	7	6	50	53
-15	19	68	68	-9	22	29	22	-1	9	42	26	7	7	87	82
-15	21	31	33	-9	25	22	23	-1	10	72	70	7	8	51	66
-15	24	25	29	-7	4	94	102	-1	11	93	90	7	10	52	50
-15	25	25	30	-7	5	257	259	-1	12	60	61	7	11	42	49

Table 7. (Continued)

H	L	FO	FC
7	13	60	56
7	15	24	18
7	19	24	26
7	21	18	18
9	4	101	98
9	5	55	58
9	6	28	22
9	7	72	73
9	8	31	25
9	9	16	13
9	11	41	47
9	12	29	29
9	13	45	41
9	19	27	20
11	4	26	24
11	5	31	26
11	7	43	43
11	8	26	26
11	9	35	27
11	10	48	41
11	11	17	22
11	12	24	26
11	13	35	29
13	4	36	43
13	5	23	23
13	6	47	54
13	7	63	66
13	8	57	53
13	9	42	40
13	10	24	28
15	4	48	56
15	5	34	34
15	6	57	52
15	7	67	60
15	8	21	21
15	9	24	28
17	4	39	37
17	5	24	27
17	7	39	41
17	13	20	18
19	5	17	23
19	7	21	25
23	0	30	36
25	0	29	26
K=	2		
-30	22	27	21
-28	12	19	17
-28	14	24	15
-26	12	27	28
-26	14	33	34
-26	18	19	18
-24	4	42	39
-24	6	19	28
-24	10	47	49
-24	12	54	64
-24	14	46	52
-24	18	27	32
-24	20	27	28
-22	5	27	23
-22	7	33	29
-22	8	29	29
-22	10	52	59
-22	12	58	61
-22	13	18	24
-22	16	55	55
-22	18	59	66
-22	20	37	46
-22	24	27	25
-20	5	37	30
-20	6	26	26
-20	11	25	22
-20	12	17	27
-20	13	52	62
-20	16	75	66
-20	18	65	61
-20	24	39	44
-18	6	24	34
-18	8	31	33
-18	10	35	37
-18	12	37	45
-18	13	40	48
-18	14	29	24
-18	16	17	18
-18	18	24	16
-18	19	35	34
-18	22	26	25
-18	24	33	39
-16	4	28	32
-16	6	60	67
-16	8	114	106
-16	9	22	25
-16	10	47	42
-16	12	49	50
-16	13	15	19
-16	14	38	41
-16	16	28	20
-16	19	38	40
-14	4	94	103
-14	5	15	18
-14	6	102	113
-14	8	126	131
-14	9	25	33
-14	10	68	76
-14	12	118	107
-14	14	85	79
-14	16	41	42
-14	18	23	32
-14	19	23	19
-14	20	38	38
-12	4	123	120
-12	5	19	15
-12	6	82	83
-12	7	64	65
-12	9	83	84
-12	10	146	137
-12	12	150	141
-12	14	61	67
-12	16	43	51
-12	18	76	78
-12	20	54	59
-12	22	36	36
-10	4	82	75
-10	5	65	56
-10	6	34	19
-10	7	82	92
-10	8	54	55
-10	9	41	41
-10	10	103	89
-10	12	137	132
-10	13	52	50
-10	14	31	31
-10	15	54	56
-10	16	83	76
-10	18	75	76
-10	20	29	40
-10	24	38	43
-8	4	148	158
-8	6	108	97
-8	7	64	58
-8	8	138	137
-8	9	31	29
-8	10	23	22
-8	11	22	28
-8	12	17	11
-8	13	106	99
-8	15	43	47
-8	16	60	65
-8	18	67	69
-8	20	34	35
-8	21	25	19
-8	24	33	41
-6	6	174	178
-6	7	45	43
-6	8	113	113
-6	9	26	24
-6	10	83	82
-6	12	41	46
-6	13	90	85
-6	14	48	44
-6	15	25	32
-6	19	38	31
-6	21	18	19
-6	24	27	34
-4	6	86	71
-4	8	120	110
-4	12	108	98
-4	14	73	69
-4	16	31	36
-4	18	24	21
-4	19	43	41
-4	20	31	15
-4	21	26	17
-2	6	125	117
-2	7	29	34
-2	8	141	127
-2	9	61	47
-2	10	93	89
-2	12	121	121
-2	14	42	48
-2	16	36	33
-2	18	35	32
-2	19	18	17
-2	20	49	49
0	6	174	182
0	7	14	15
0	8	122	104
0	9	87	78
0	10	93	102
0	11	23	18
0	12	141	132
0	14	57	57
0	18	65	65
0	20	38	48
2	4	82	83
2	5	37	34
2	7	100	85
2	8	56	66
2	9	49	59
2	10	77	92
2	11	25	38
2	12	84	85
2	14	33	26
2	15	38	34
2	16	43	46
2	18	53	64
2	20	27	31
4	4	183	169
4	5	78	83
4	6	42	34
4	7	93	105
4	8	81	75
4	9	25	35
4	10	30	42
4	11	22	22

Table 7. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
4	12	40	54	-23	5	20	25	-15	11	51	57	-9	15	17	6
4	13	56	53	-23	8	34	27	-15	12	15	21	-9	16	84	85
4	15	44	46	-23	9	19	15	-15	13	50	54	-9	17	46	42
4	18	27	26	-23	10	58	53	-15	15	35	42	-9	18	58	60
6	4	32	40	-23	11	33	34	-15	16	42	41	-9	19	50	56
6	6	124	128	-23	12	38	48	-15	19	51	55	-9	20	24	24
6	8	127	121	-23	13	43	45	-15	21	31	33	-9	21	36	37
6	10	40	54	-23	16	27	22	-15	25	28	15	-9	25	28	31
6	11	31	30	-23	18	33	33	-13	4	67	59	-7	7	88	86
6	12	17	15	-23	19	27	33	-13	5	102	96	-7	8	15	7
6	13	40	44	-23	20	27	24	-13	6	71	70	-7	10	83	81
6	14	48	38	-23	21	19	23	-13	7	83	78	-7	11	23	17
6	16	27	24	-21	4	34	29	-13	10	76	73	-7	12	53	63
8	4	123	121	-21	6	27	25	-13	11	51	42	-7	13	55	61
8	6	138	140	-21	8	18	17	-13	12	71	61	-7	15	45	35
8	8	57	65	-21	9	29	25	-13	13	35	34	-7	16	36	38
8	10	27	9	-21	10	26	23	-13	14	50	56	-7	17	22	24
8	12	63	61	-21	11	41	34	-13	15	38	36	-7	18	23	17
8	14	53	57	-21	13	41	44	-13	16	26	34	-7	19	24	31
10	4	83	86	-21	14	36	24	-13	17	25	36	-7	21	25	11
10	6	70	73	-21	16	58	49	-13	18	23	31	-7	22	26	27
10	8	30	22	-21	17	45	42	-13	19	47	45	-7	25	28	27
10	9	18	9	-21	18	41	36	-13	20	30	32	-5	8	60	62
10	10	36	35	-21	19	46	48	-13	21	17	20	-5	9	17	13
10	12	63	68	-21	21	19	19	-13	25	28	26	-5	10	97	102
10	14	33	35	-21	24	20	24	-11	4	20	20	-5	11	14	9
12	4	17	4	-19	5	18	26	-11	5	16	20	-5	12	12	14
12	6	25	18	-19	6	31	30	-11	6	16	18	-5	13	65	56
12	9	26	29	-19	8	39	38	-11	7	23	21	-5	14	39	39
12	10	27	27	-19	10	30	25	-11	8	51	40	-5	15	32	34
12	12	43	39	-19	16	30	28	-11	9	41	41	-5	16	34	43
12	18	26	23	-19	17	35	34	-11	10	117	104	-5	17	16	13
14	4	28	41	-19	19	25	32	-11	11	72	67	-5	19	17	20
14	5	22	22	-19	22	27	26	-11	12	96	97	-5	21	18	12
14	7	38	34	-19	23	23	23	-11	13	76	75	-3	8	57	64
14	9	19	19	-19	24	28	33	-11	14	37	42	-3	9	88	83
16	4	26	32	-19	25	31	30	-11	15	38	37	-3	10	35	36
16	8	28	25	-17	5	51	48	-11	16	47	48	-3	11	50	45
18	6	39	36	-17	6	37	37	-11	17	31	31	-3	12	100	100
18	8	34	37	-17	7	37	32	-11	18	64	68	-3	13	47	52
20	6	34	37	-17	8	32	34	-11	19	37	37	-3	14	38	43
				-17	9	54	59	-11	20	38	46	-3	15	30	34
	K=	3		-17	12	22	24	-11	21	25	31	-3	16	35	35
				-17	13	51	50	-11	25	28	25	-3	17	37	26
-25	4	25	26	-17	14	23	18	-9	4	22	18	-3	19	40	34
-25	5	21	27	-17	15	46	37	-9	5	22	15	-3	21	19	25
-25	6	36	33	-17	19	17	23	-9	6	30	37	-1	7	70	75
-25	7	29	21	-17	22	26	27	-9	7	66	71	-1	8	37	38
-25	10	20	27	-15	4	45	39	-9	8	17	21	-1	9	11	17
-25	12	34	38	-15	5	51	50	-9	9	30	39	-1	10	76	64
-25	14	28	26	-15	6	81	70	-9	10	68	60	-1	11	78	82
-25	15	28	25	-15	7	52	43	-9	11	17	21	-1	12	80	72
-25	19	20	20	-15	8	65	53	-9	12	28	28	-1	13	65	64
-25	25	20	10	-15	9	36	41	-9	13	55	63	-1	14	26	24

Table 7. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
-1	15	42	42	3	6	50	50	5	13	17	9	9	13	39	42
-1	18	25	33	3	7	34	23	5	15	29	20	9	14	20	33
-1	19	45	51	3	8	17	16	7	5	112	98	9	15	20	17
-1	21	19	26	3	9	38	24	7	6	85	77	11	4	65	70
1	6	28	45	3	15	25	20	7	7	69	64	11	5	44	50
1	7	29	39	3	16	45	49	7	8	41	51	11	6	30	33
1	9	17	20	3	18	27	39	7	10	48	45	11	7	25	21
1	10	91	80	3	20	20	16	7	13	45	39	11	8	26	24
1	11	37	41	5	4	71	80	7	14	19	19	11	10	33	35
1	12	55	69	5	5	45	48	7	15	34	29	11	11	19	25
1	13	27	30	5	6	30	38	9	4	67	59	11	12	40	46
1	14	51	50	5	7	94	81	9	5	53	63	11	13	20	25
1	15	24	17	5	8	57	46	9	6	35	39	13	10	28	32
1	16	35	27	5	9	33	35	9	7	33	32	15	4	53	65
1	17	40	39	5	10	54	58	9	8	48	50	15	6	27	21
1	18	26	37	5	11	28	35	9	11	32	26	17	4	31	33
1	19	38	40	5	12	27	40	9	12	47	49	17	7	41	30
3	5	26	23												

Crystallographic Data for Ni(EIA)(CH_3OH)

A well-shaped green crystal of Ni(EIA)(CH_3OH) was mounted and precession photographs were taken, using zirconium-filtered Mo Kα radiation, λ = 0.7106Å. The crystal was found to be orthorhombic with a = 25.84(2)Å, b = 13.12(2)Å and c = 12.29(2)Å. The density calculated on the basis of 16 monomer formula weights of Ni(EIA)(CH_3OH) per unit cell, 1.49 g/cm^3, agrees well with the experimental value, 1.49(1) g/cm^3, obtained by the flotation method using a solution of zinc chloride, $ZnCl_2$, in water. The crystals of Ni(EIA)(CH_3OH) dissolve slowly in water, but repeated determinations of the density were within 0.006 g/cm^3 of one another.

The systematic absence of the reflections with $h = 2n + 1$ on the $h00$ zone, the systematic absence of the reflections with $k = 2n + 1$ on the $0k0$ zone and the systematic absence of the reflections with $l = 2n + 1$ on the $00l$ zone were consistent only with the space group $P2_12_12_1$ (No. 19).

Several attempts were made to mount a crystal in such a way that it would remain stable for a long enough period of time to collect three-dimensional X-ray data on the Picker diffractometer. It was known that the crystal decomposed through the loss of methanol. The attempts of data collection involved trying to form a seal around the crystal so that it could not lose this methanol. All crystals used were the larger crystals, because they stayed stable a longer period of time in air. One method tried was to mount the crystal on a glass rod with Duco cement. After this had dried approximately 15 minutes, the crystal and

glass rod were dipped in a solution of Avon clear fingernail polish thinned with ethyl acetate. After this dried approximately 15 minutes, the crystal was redipped. After about two days small cracks developed in the seal and the crystal decomposed. Another method involved sealing the crystal in a Lindemann glass capillary tube. The crystal decomposed again in about two days. It was also attempted to seal the crystal in a capillary with a methanol atmosphere inside the capillary. The methanol attacked the Duco cement and transformed the cement and crystal into an amorphous mass. An attempt was made to glue the crystal to a glass rod with epoxy cement but by the time the epoxy was dry the crystal had decomposed in the air. If it was sealed immediately, the epoxy never cured. Therefore, although hope was raised several times the author was never able to achieve more than the alignment of the diffractometer with this crystal.

Solution of the Structure of $[Ni(EIA)]_2$ (41)

A red needle crystal with dimensions 0.10 x 0.17 x 0.44 mm was mounted on the precession camera with the long dimension along the spindle axis. Viewed from the end the crystal is a parallelogram Each perpendicular distance from one side to the opposite side was equal to 0.10 mm. The long diagonal distance across the face on the end was equal to 0.17 mm. Orientation precession photographs were taken, using zirconium-filtered Mo Kα radiation, λ = 0.7107Å. Optical examination and precession photographs indicated a monoclinic cell. The precession photograph values for the unit cell parameters are a = 17.04(3)Å, b = 7.45(1)Å, c = 14.04(2)Å, β = 113.00(10)°, and V = 1640Å^3. The

absence of hkl reflections with $h + k = 2n + 1$ and the absence of $h0l$ reflections with $l = 2n + 1$ indicated space group Cc (No. 9) or C2/c (No. 15). The space group ambiguity was resolved in favor of C2/c through the Patterson map and the successful refinement of the structure.

The same crystal and goniometer head used for space group determination were transferred to the automated Picker four-circle diffractometer. Since the alignment on the diffractometer was more critical than on the precession camera, the crystal was realigned according to published instructions (52). The four angles (ϕ, χ, ω and 2θ) which define the position of the crystal and counter to record a reflection in reciprocal space, were determined for five reflections. From these five reflections, refined unit cell parameters and angle settings for the remaining data were obtained by a least-squares method using a computer program modified for the Univac 1108 computer by Bertrand and Kirkwood (53). The cell parameters obtained from the diffractometer data are a = 16.99(2)Å, b = 7.45(1)Å, c = 14.02(2)Å, β = 112.93(4)° and V = 1634Å at 25°C, using Mo radiation, λ = 0.7107Å.

The calculated density of 1.62 g/cm^3 for eight formula units (four dimers) per unit cell agrees well with the observed experimental density of 1.61(1) g/cm^3 measured by the flotation method using a mixture of carbon tetrachloride and 1,3-diiodopropane.

The X-ray intensity measurements were made, using the same crystal as used for the cell measurements, with molybdenum radiation. The intensities were collected by the θ - 2θ scan technique with a

takeoff angle of 1.6° and a scan rate of one degree per minute. Below $2\theta = 32°$, a symmetrical scan of 1.5° was taken about the calculated position for each reflection; above $2\theta = 32°$, a symmetrical scan of two degrees was used. When the scan was completed stationary background counts of 15 and 20 seconds for the 1.5 and two degree scans, respectively, were taken at the beginning (hereafter referred to as bgd1) and at the end (hereafter referred to as bgd2) of the scan. Calibrated copper attenuators were used in the collection of data. The attenuators were calibrated by collecting intensities on 30 different reflections of various magnitudes. The threshold point was set so that attenuators would be inserted automatically and recorded when the counting rate exceeded 10,000 counts per second. The pulse height analyzer was set for approximately a 90 per cent window, centered on the Mo Kα peak. A total of 1769 reflections were collected, including the equivalent $hk0$ and $\bar{h}k0$ reflections which were later averaged. Corrected intensities (CI) were obtained by subtracting three times the actual measured background from the total integrated peak count (CT) as specified by the equation

$$CI = CT - 3(bgd1 + bgd2)$$

where the variables are already defined. The factor of three in the calculation arises from the peak scan time being three times as long as the background counting time. The corrected intensities were assigned standard deviations (54) according to the formula

$$\sigma(I) = [CT + 0.25(tc/tb)^2(bdg1 + bdg2)]^{1/2}$$

where tc is the scan time and tb is the counting time of each background (either bgd1 or bgd2). A total of 884 reflections were accepted as statistically above background on the basis that $\sigma(I)/CI$ be less than 0.18. The intensities were corrected for Lorentz and polarization effects but were not corrected for absorption. The calculated linear absorption coefficient for molybdenum radiation, μ, is 23.1 cm^{-1}. For the $0k0$ reflections, rotation around ϕ did not cause more than 5 per cent variation in intensity. Periodic checks of standard reflections showed no significant variation. The reflections collected were in the region between -14 to 14 in h, 0 to 10 in k and 0 to 10 in l. Computations were carried out as described earlier.

A three-dimensional Patterson function was calculated using the 884 unique nonzero reflections. The distribution of peaks on the Patterson map was consistent with the centrosymmetric space group, C2/c. All atoms were placed in the Wyckoff set 8f .

Positions for the nickel atoms and for the atoms coordinated to nickel were obtained from the Patterson function. A subsequent electron density calculation phased on these atoms revealed the positions of all carbon atoms. After one cycle of least-squares refinement of the scale factor alone; a second cycle varying scale factor and atomic coordinates; and four further cycles in which scale factor, coordinates and isotropic temperature factors were allowed to vary, the refinement converged to a conventional R_1 value of 0.079. At this point with all

reflections weighted at unity, the value of R_2 was 0.084.

After further refinement with anisotropic temperature factors, weights (w_i) were assigned to each reflection in the refinement process by the formula

$$w_i = 4(CI)/ (I)^2$$

where the variables have been previously defined. With these further calculations the refinement converged to a conventional R_1 value of 0.079 and a weighted R_2 value of 0.044. A difference electron density map at this point revealed peaks for ten of the 11 hydrogen atoms of the ligand. The three-dimensional difference electron density around each hydrogen position was run in thousanths of a unit cell. From this, positions near the maximum electron density were picked as the atomic positions for the ten hydrogens which were found. A position was calculated for the eleventh hydrogen -- the one attached to the C7 carbon -- assuming a carbon to hydrogen distance of 1.06Å. All hydrogen atoms were introduced into the structure factor calculations at the coordinates listed in Table 8. Each hydrogen atom was assigned the isotropic temperature factor of the adjacent carbon. Further refinement of all parameters except hydrogen coordinates and hydrogen temperature factors converged to a conventional R_1 value of 0.066 and a weighted R_2 value of 0.034. In the final cycle of refinement, there was no parameter shift greater than 1/10 of one esd. The final difference Fourier had no positive maxima greater than 0.5e/Å^3.

In the structure factor calculations, the scattering factors tabulated by Ibers (51) were employed for all atoms.

The positional and isotropic thermal parameters derived from the last cycle of least-squares refinement are presented in Table 8, and the anisotropic thermal parameters are given in Table 9. The observed and calculated structure factors for the 884 nonzero unique reflections are given in Table 10.

Table 8. Final Positional and Thermal Parameters for $[Ni(EIA)]_2$

Atom	x	y	z	B, A^2
Ni1	0.4570(1)	0.1836(2)	0.3128(1)	2.27(3)
O2	0.5658(3)	0.1200(6)	0.3256(4)	2.69(14)
N3	0.5007(4)	0.2371(9)	0.4526(5)	2.28(17)
O4	0.3464(3)	0.2339(8)	0.2876(5)	3.36(16)
C5	0.4990(5)	0.3029(15)	0.6213(5)	4.05(25)
C6	0.4578(6)	0.2804(12)	0.5061(7)	2.85(21)
C7	0.3665(6)	0.3046(15)	0.4592(7)	3.76(24)
C8	0.3182(6)	0.2805(12)	0.3569(8)	3.20(23)
C9	0.2227(5)	0.3140(18)	0.3152(6)	5.04(30)
C10	0.5952(5)	0.2036(12)	0.4994(6)	3.06(21)
C11	0.6277(5)	0.2162(11)	0.4140(6)	3.31(23)
H1C5	0.57	0.40	0.63	
H2C5	0.54	0.17	0.67	
H3C5	0.49	0.38	0.67	
H4C7	0.334	0.340	0.508	
H5C9	0.20	0.26	0.37	
H6C9	0.20	0.46	0.27	
H7C9	0.62	0.32	0.55	
H8C10	0.60	0.06	0.51	
H9C10	0.64	0.36	0.39	
H10C11	0.68	0.12	0.42	
H11C11	0.19	0.26	0.25	

Table 9. Final Anisotropic Thermal Parameters ($X10^4$) for $[Ni(EIA)]_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni1	22(1)	125(2)	33(1)	2(1)	7(1)	-1(2)
O2	33(3)	88(12)	38(4)	10(5)	5(3)	5(6)
N3	33(4)	186(23)	31(5)	17(6)	8(4)	1(8)
O4	29(3)	240(21)	42(4)	12(5)	12(3)	3(7)
C5	53(5)	223(23)	14(5)	36(11)	10(4)	-14(12)
C6	47(6)	82(23)	49(7)	33(8)	19(6)	26(9)
C7	50(6)	161(22)	44(7)	30(11)	18(5)	-7(14)
C8	46(6)	152(26)	46(7)	25(9)	26(6)	26(11)
C9	34(5)	453(32)	42(6)	61(13)	13(4)	38(16)
C10	24(4)	63(18)	65(7)	6(8)	-2(4)	6(11)
C11	35(4)	91(21)	48(6)	-10(8)	16(5)	1(9)

Table 10. Observed and Calculated Structure Factors for $[Ni(EIA)]_2$

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
	L=	0		14	8	145	115	-2	4	719	776	-14	10	113	44
				1	9	117	67	0	4	617	625	-12	10	115	71
4	0	317	331	5	9	103	51	2	4	507	539	-8	10	110	89
6	0	295	247	11	9	115	80	4	4	364	375	2	10	143	131
8	0	287	271	13	9	133	99	6	4	293	323	4	10	126	116
10	0	529	541	2	10	118	62	8	4	81	35	12	10	122	71
12	0	399	383	12	10	119	53	10	4	279	295	14	10	120	86
14	0	168	154					12	4	309	299				
3	1	246	246		L=	1		14	4	207	193		L=	2	
5	1	68	61					-13	5	126	113				
7	1	325	281	-13	1	212	205	-11	5	201	203	-12	0	372	363
9	1	224	237	-11	1	441	472	-9	5	219	210	-10	0	688	684
11	1	215	219	-9	1	955	952	-7	5	177	192	-8	0	1194	1204
13	1	109	100	-7	1	566	568	-5	5	94	81	-6	0	511	523
0	2	2078	2078	-5	1	332	245	-3	5	196	230	-4	0	135	115
2	2	747	706	-3	1	137	98	-1	5	193	197	-2	0	294	317
4	2	199	192	3	1	160	185	1	5	200	201	0	0	429	405
6	2	374	336	5	1	246	263	3	5	281	311	2	0	358	347
8	2	82	37	7	1	494	410	7	5	151	160	6	0	389	405
10	2	299	293	9	1	370	348	9	5	112	82	8	0	77	54
12	2	251	233	11	1	387	374	11	5	114	107	10	0	401	357
14	2	122	121	13	1	345	352	13	5	138	137	12	0	193	175
1	3	775	814	-14	2	134	105	-14	6	108	73	14	0	230	236
3	3	446	414	-12	2	244	257	-12	6	107	87	-11	1	317	296
7	3	372	357	-10	2	485	477	-10	6	118	115	-9	1	393	376
9	3	339	357	-8	2	472	452	-2	6	260	286	-7	1	338	335
11	3	402	414	-6	2	324	328	0	6	187	187	-5	1	74	99
13	3	227	231	-4	2	202	198	2	6	139	141	-1	1	551	515
0	4	231	273	-2	2	1063	1107	4	6	160	148	3	1	256	229
2	4	83	70	0	2	831	850	6	6	169	191	5	1	209	192
6	4	272	283	2	2	658	630	8	6	97	43	7	1	72	61
8	4	175	185	4	2	290	268	10	6	143	131	9	1	78	40
10	4	98	70	6	2	181	168	12	6	161	148	11	1	139	125
1	5	333	371	8	2	170	148	14	6	120	81	13	1	111	81
3	5	228	208	10	2	273	281	-13	7	145	142	-12	2	166	176
5	5	88	38	12	2	252	228	-11	7	184	203	-10	2	338	341
7	5	102	89	14	2	153	135	-9	7	215	246	-8	2	721	691
9	5	139	128	-11	3	90	63	-7	7	157	171	-6	2	321	314
11	5	241	255	-9	3	210	218	-5	7	114	84	-4	2	105	92
13	5	173	168	-7	3	81	52	-3	7	116	112	-2	2	452	464
0	6	259	256	-3	3	237	221	-1	7	161	160	0	2	144	116
2	6	238	258	-1	3	132	140	1	7	236	246	2	2	197	197
4	6	137	159	1	3	430	398	3	7	243	289	4	2	347	305
6	6	101	96	5	3	249	246	5	7	144	138	6	2	371	378
8	6	139	141	7	3	395	394	9	7	105	87	8	2	80	62
10	6	186	185	9	3	96	72	11	7	180	168	10	2	308	293
12	6	202	211	11	3	162	140	13	7	207	223	12	2	168	140
14	6	156	129	13	3	148	137	2	8	120	99	14	2	176	167
0	8	228	259	-14	4	166	148	-11	9	118	98	-13	3	182	185
2	8	163	182	-12	4	231	246	-9	9	121	122	-11	3	483	501
4	8	109	88	-10	4	370	390	1	9	146	121	-9	3	608	622
8	8	114	66	-8	4	288	304	3	9	115	115	-7	3	549	574
10	8	138	122	-6	4	217	237	5	9	111	66	-5	3	310	293
12	8	173	168	-4	4	111	103	13	9	126	119	-1	3	715	689

Table 10. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
1	3	517	501	8	8	104	49	-6	4	484	544	-6	0	692	692
3	3	577	562	12	8	117	109	-4	4	545	595	-4	0	721	706
5	3	528	532	14	8	136	122	-2	4	369	364	-2	0	479	395
7	3	243	215	-3	9	105	24	0	4	165	171	0	0	108	127
9	3	99	87	1	9	120	109	2	4	504	534	2	0	481	526
11	3	312	314	3	9	138	123	4	4	504	517	4	0	275	316
13	3	208	217	5	9	134	87	6	4	403	425	6	0	442	417
-12	4	90	78	13	9	122	53	8	4	148	139	8	0	650	610
-10	4	130	105	-8	10	110	60	12	4	171	163	10	0	152	122
-4	4	127	118	2	10	111	57	14	4	195	193	14	0	172	161
-2	4	416	411					-11	5	105	104	-9	1	211	217
0	4	219	220		L=	3		-9	5	159	137	-7	1	224	191
2	4	182	178					-7	5	190	181	-3	1	195	198
4	4	176	145	-11	1	293	270	-5	5	199	206	1	1	87	33
6	4	106	109	-9	1	617	614	-3	5	89	50	3	1	200	179
10	4	144	125	-7	1	671	697	-1	5	151	162	5	1	151	169
-13	5	109	119	-5	1	389	338	1	5	119	125	7	1	243	221
-11	5	257	282	-3	1	148	77	3	5	249	254	9	1	229	218
-9	5	314	339	-1	1	370	349	5	5	291	285	11	1	141	119
-7	5	292	313	1	1	706	659	7	5	142	136	-14	2	172	146
-5	5	256	254	3	1	559	505	9	5	153	130	-10	2	192	199
-3	5	118	131	5	1	454	446	-10	6	159	175	-8	2	537	542
-1	5	278	284	7	1	355	346	-8	6	205	229	-6	2	488	499
1	5	267	274	9	1	99	68	-6	6	198	234	-4	2	540	523
3	5	401	428	11	1	95	59	-4	6	302	342	-2	2	352	333
5	5	560	472	13	1	103	54	-2	6	230	247	0	2	175	174
7	5	222	214	-12	2	144	150	2	6	213	244	2	2	542	527
9	5	103	81	-10	2	537	552	4	6	266	280	4	2	276	269
11	5	285	287	-8	2	527	564	6	6	189	202	6	2	280	268
13	5	177	198	-6	2	447	461	14	6	115	95	8	2	369	368
-12	6	141	126	-4	2	393	392	-9	7	149	148	14	2	107	104
-10	6	182	192	-2	2	264	197	-7	7	222	244	-13	3	197	197
-8	6	224	244	0	2	188	193	-5	7	236	283	-9	3	369	392
-6	6	195	216	2	2	473	418	-3	7	98	77	-7	3	448	456
-2	6	159	156	4	2	300	318	1	7	185	204	-5	3	280	288
0	6	228	233	6	2	304	320	3	7	332	363	-3	3	516	534
2	6	339	360	8	2	149	148	5	7	325	361	-1	3	140	109
4	6	395	434	10	2	104	83	7	7	159	186	1	3	235	195
6	6	170	165	12	2	96	93	9	7	98	62	3	3	502	482
12	6	127	133	14	2	147	155	-7	9	118	116	5	3	396	413
14	6	166	147	-9	3	130	141	1	9	108	98	7	3	422	417
-9	7	103	83	-7	3	224	232	3	9	154	182	9	3	371	378
-5	7	104	54	-5	3	145	154	5	9	159	176	11	3	212	194
5	7	119	119	-3	3	222	217	2	10	111	112	-12	4	97	89
11	7	126	113	-1	3	329	323	4	10	137	107	-8	4	77	34
13	7	105	50	1	3	254	257	6	10	129	94	0	4	159	144
-12	8	119	84	3	3	194	204	14	10	117	50	2	4	261	262
-10	8	111	114	5	3	152	139					10	4	102	99
-8	8	159	179	7	3	140	115		L=	4		-13	5	200	218
-6	8	126	143	9	3	165	143					-11	5	130	152
0	8	125	134	11	3	119	113	-14	0	201	179	-9	5	225	242
2	8	216	235	-12	4	104	60	-12	0	90	87	-7	5	299	342
4	8	274	299	-10	4	439	462	-10	0	335	383	-5	5	260	294
6	8	153	163	-8	4	512	540	-8	0	843	825	-3	5	428	467

Table 10. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-1	5	121	95	-2	2	515	528	-5	7	289	342	-11	3	240	226
1	5	222	228	0	2	325	315	-3	7	256	275	-7	3	181	152
5	5	313	323	2	2	203	132	-1	7	157	156	-5	3	369	382
7	5	247	253	4	2	133	130	5	7	173	182	-3	3	584	610
9	5	212	217	6	2	408	380	7	7	159	169	-1	3	519	527
11	5	129	131	8	2	374	348	9	7	148	128	1	3	345	338
-14	6	117	94	10	2	290	279	-6	8	116	117	5	3	266	254
-8	6	212	218	12	2	102	63	-4	8	134	110	7	3	474	471
-6	6	320	365	14	2	113	68	4	8	101	67	9	3	273	277
-4	6	324	370	-13	3	297	319	-5	9	139	169	11	3	179	165
-2	6	151	141	-11	3	87	94	-3	9	126	131	13	3	100	65
4	6	211	247	-9	3	93	103	-1	9	107	75	0	4	109	109
6	6	208	219	-7	3	113	105	5	9	108	86	2	4	134	130
8	6	137	141	-5	3	164	155	-6	10	142	165	6	4	111	96
10	6	104	64	-3	3	221	208	-4	10	137	148	14	4	107	57
14	6	108	89	-1	3	78	67	-2	10	116	88	-13	5	132	147
-11	7	118	99	1	3	387	374	6	10	120	77	-11	5	146	145
-3	7	142	135	3	3	271	253					-7	5	210	206
1	7	99	74	5	3	137	118		L=	6		-5	5	277	296
-8	8	166	176	7	3	284	281					-3	5	343	384
-6	8	236	280	9	3	230	241	-14	0	412	420	-1	5	234	244
-4	8	227	274	-14	4	220	242	-12	0	441	464	1	5	101	76
-2	8	108	119	-12	4	238	253	-10	0	118	175	5	5	149	154
4	8	167	185	-8	4	311	345	-8	0	81	52	7	5	264	280
6	8	148	154	-6	4	401	443	-6	0	243	149	9	5	124	135
14	8	115	73	-4	4	358	379	-4	0	788	742	11	5	102	80
-7	9	128	116	-2	4	465	519	-2	0	1050	1016	-14	6	172	173
-5	9	119	149	0	4	149	159	0	0	929	881	-12	6	131	129
3	9	113	104	4	4	164	202	2	0	152	149	-6	6	174	193
5	9	110	106	6	4	373	373	6	0	375	358	-4	6	257	291
7	9	118	79	8	4	306	296	8	0	716	685	-2	6	231	246
-6	10	112	88	10	4	233	236	10	0	377	375	0	6	188	210
				14	4	108	66	12	0	126	117	4	6	103	90
	L=	5		-9	5	97	25	-11	1	127	113	6	6	161	152
				-7	5	154	152	-9	1	83	63	8	6	145	145
-13	1	509	527	-5	5	215	250	-5	1	134	148	10	6	134	131
-11	1	77	72	-3	5	202	197	-3	1	340	323	7	7	113	73
-9	1	215	194	-1	5	163	167	-1	1	352	334	-14	8	149	166
-7	1	198	186	1	5	167	179	1	1	227	258	-12	8	111	111
-5	1	326	384	5	5	137	155	5	1	167	139	-6	8	127	130
-3	1	556	563	7	5	112	93	7	1	279	266	-4	8	183	218
-1	1	509	485	9	5	108	70	9	1	168	168	-2	8	177	189
1	1	456	351	-14	6	125	123	11	1	122	94	0	8	141	143
3	1	307	268	-12	6	151	143	-14	2	305	318	8	8	123	108
5	1	424	407	-8	6	158	185	-12	2	345	345	10	8	116	93
7	1	792	777	-6	6	153	169	-10	2	86	80	-13	9	109	94
9	1	700	684	-4	6	132	140	-4	2	502	482	-5	9	126	126
11	1	176	163	-2	6	159	204	-2	2	623	593	-3	9	127	87
-14	2	157	162	2	6	98	74	0	2	447	432	-1	9	116	72
-12	2	163	152	6	6	137	140	6	2	193	167				
-10	2	80	65	8	6	109	99	8	2	442	414		L=	7	
-8	2	245	247	10	6	112	82	10	2	222	207				
-6	2	292	313	-13	7	144	144	12	2	99	64	-13	1	262	247
-4	2	247	244	-7	7	191	225	-13	3	178	184	-11	1	362	387

Table 10. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
-9	1	241	256	9	5	126	131	11	1	108	86	10	6	134	125
-5	1	341	306	11	5	139	130	-12	2	346	342	12	6	152	133
-3	1	840	814	-14	6	133	128	-10	2	347	353	-14	8	112	114
-1	1	903	911	-12	6	98	74	-6	2	91	84	-12	8	142	156
1	1	658	618	-10	6	129	127	-4	2	190	191	-10	8	134	160
3	1	306	287	-6	6	151	150	-2	2	212	211	-8	8	128	111
9	1	280	260	-4	6	171	177	0	2	351	339	0	8	125	124
11	1	128	141	-2	6	221	237	2	2	245	245	2	8	115	130
13	1	127	106	0	6	107	69	4	2	155	132				
-14	2	197	223	8	6	129	101	8	2	108	72		L=	9	
-12	2	260	258	-13	7	175	195	10	2	151	135				
-10	2	362	382	-11	7	137	155	12	2	145	112	-13	1	268	285
-8	2	293	295	-9	7	112	115	14	2	127	74	-11	1	551	581
-6	2	124	111	-5	7	148	142	-13	3	253	280	-9	1	425	416
-4	2	398	403	-3	7	186	212	-11	3	417	460	-7	1	88	84
-2	2	671	686	-1	7	192	229	-9	3	347	362	-5	1	137	143
0	2	453	432	1	7	166	167	-7	3	129	135	-3	1	299	287
2	2	263	274	3	7	97	56	-5	3	214	221	-1	1	474	441
6	2	242	245	9	7	114	121	-3	3	437	438	1	1	491	478
8	2	318	305	11	7	145	138	-1	3	643	637	3	1	344	351
10	2	208	202	-12	8	107	62	1	3	466	470	5	1	131	98
12	2	142	137	-3	9	109	103	3	3	311	307	9	1	180	144
14	2	106	71	-1	9	119	101	5	3	192	180	11	1	150	145
-11	3	95	83	1	9	127	85	7	3	122	113	13	1	152	118
-7	3	140	125	-14	10	119	87	9	3	193	172	-14	2	170	161
-5	3	101	112	-12	10	119	87	11	3	188	180	-12	2	318	353
-3	3	210	218	2	10	112	53	13	3	131	128	-10	2	398	447
-1	3	187	192					-14	4	139	122	-8	2	287	305
1	3	129	112		L=	8		-10	4	105	104	-6	2	149	164
3	3	127	104					-8	4	222	229	-2	2	264	276
5	3	134	118	-12	0	571	582	-6	4	86	82	0	2	383	380
-14	4	264	284	-10	0	660	677	-2	4	122	104	2	2	264	271
-12	4	247	262	-8	0	175	215	0	4	108	102	4	2	123	122
-10	4	311	332	-4	0	368	390	6	4	96	79	6	2	104	73
-8	4	169	169	-2	0	443	476	-13	5	164	185	10	2	121	105
-6	4	208	217	0	0	654	659	-11	5	233	270	12	2	125	98
-4	4	384	406	2	0	425	410	-9	5	173	176	-11	3	177	179
-2	4	558	595	4	0	154	147	-5	5	137	141	-5	3	135	141
0	4	322	315	6	0	118	94	-3	5	206	207	-1	3	104	89
2	4	211	211	8	0	193	171	-1	5	344	357	1	3	124	130
6	4	200	193	10	0	242	224	1	5	264	279	3	3	130	130
8	4	261	269	12	0	185	181	3	5	237	243	9	3	100	69
10	4	192	194	14	0	125	99	5	5	198	198	11	3	117	76
12	4	168	160	-13	1	147	141	9	5	119	111	-14	4	165	171
14	4	151	113	-11	1	254	259	11	5	149	141	-12	4	294	321
-13	5	155	167	-9	1	231	228	13	5	131	124	-10	4	350	385
-11	5	126	137	-7	1	111	108	-14	6	138	174	-8	4	239	255
-9	5	148	165	-5	1	130	126	-12	6	180	212	-6	4	187	196
-5	5	111	105	-3	1	284	278	-10	6	212	234	-4	4	167	173
-3	5	163	173	-1	1	414	379	-8	6	184	204	-2	4	161	170
-1	5	204	215	1	1	285	262	-4	6	115	101	0	4	355	371
1	5	189	171	3	1	159	138	-2	6	125	126	2	4	296	314
5	5	133	117	7	1	108	81	0	6	193	209	4	4	201	199
7	5	131	131	9	1	118	92	2	6	156	167	6	4	147	136

Table 10. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
8	4	100	62	0	0	379	375	-11	5	142	145	1	5	105	90
10	4	139	132	2	0	224	224	-9	5	180	183				
12	4	149	138	4	0	291	297	-7	5	223	249		L=12		
14	4	130	111	6	0	151	145	-5	5	207	225				
-13	5	102	81	10	0	130	95	-3	5	180	162	-4	0	305	313
-11	5	111	85	12	0	106	109	-1	5	146	152	-2	0	124	130
-9	5	201	207	14	0	153	130	1	5	209	216	4	0	290	285
-7	5	153	163	-13	1	96	99	3	5	128	131	-5	1	101	93
-3	5	121	110	-11	1	197	188	5	5	119	128	-3	1	101	96
-1	5	134	116	-9	1	192	193	7	5	116	77	-1	1	136	80
1	5	187	174	-7	1	167	162	-10	6	100	98	5	1	120	102
3	5	150	144	-1	1	143	138	-8	6	176	191	-4	2	214	219
-14	6	107	70	1	1	153	128	-6	6	135	125	4	2	220	202
-12	6	112	128	3	1	101	70	0	6	145	143	-5	3	212	232
-10	6	134	142	-12	2	242	252	2	6	184	192	-3	3	199	196
-6	6	103	87	-10	2	315	322	4	6	166	173	-1	3	154	132
-4	6	160	164	-8	2	284	286	6	6	110	91	3	3	176	187
0	6	152	157	-6	2	385	406	-8	8	147	145	5	3	216	214
2	6	134	130	-4	2	279	282	-6	8	147	137	-5	5	174	177
4	6	133	103	-2	2	188	169	0	8	115	115	-3	5	153	120
6	6	134	100	0	2	257	243	2	8	147	159	3	5	159	161
10	6	107	67	2	2	168	150	4	8	144	149	5	5	166	165
12	6	127	73	4	2	219	216	6	8	111	76				
-13	7	103	104	6	2	113	98	1	9	113	74		L=13		
-11	7	123	112	10	2	126	91	3	9	118	116				
-9	7	159	175	14	2	127	91					-5	1	174	165
-7	7	126	125	-13	3	153	155		L=11			-3	1	343	345
-1	7	111	120	-11	3	308	307					-1	1	194	185
1	7	194	222	-9	3	328	343	-5	1	542	528	3	1	130	94
3	7	193	222	-7	3	327	345	-3	1	163	136	5	1	182	173
5	7	117	113	-5	3	229	212	-1	1	132	95	-4	2	210	207
3	9	130	118	-3	3	139	102	3	1	131	116	-2	2	217	224
2	10	128	93	-1	3	253	252	5	1	306	301	0	2	141	118
				1	3	285	286	2	2	159	144	4	2	138	121
	L=10			3	3	191	182	4	2	163	151	-3	3	120	99
				5	3	162	158	-5	3	297	296	-4	4	218	229
-12	0	394	432	7	3	119	102	-3	3	97	96	-2	4	208	216
-10	0	519	536	13	3	124	90	5	3	147	121	4	4	165	138
-8	0	470	486	-6	4	128	103	0	4	151	134	-5	5	134	143
-6	0	512	527	-4	4	166	174	2	4	205	208	-3	5	121	107
-4	0	269	270	-13	5	104	84	4	4	192	193	-1	5	140	123
-2	0	319	308												

Crystallographic Data for $[Co(EIA)]_4$

The X-ray powder-diffraction patterns were exposed in a type 52056 Philips Company powder camera using a Norelco-Philips constant potential X-ray generator source. Ilford Industrial-G X-ray film was used for all powder patterns. Zirconium-filtered molybdenum radiation was used.

Powder-diffraction patterns were taken of Bertrand and Kelley's copper cubane type structure (36), $[Cu(EIA)]_4$, the desolvated red $[Ni(EIA)]_2$ and the unsolvated cobalt cubane type structure, $[Co(EIA)]_4$, reported here. The powder-diffraction patterns of the copper and cobalt compounds were identical in every respect. The powder pattern of the desolvated nickel compound differed markedly from both the copper and cobalt. Therefore the cobalt compound was assumed to have a cubane-type structure similar to the copper cubane.

Crystallographic Data for $Cu(NH_2CH_2CH_2CH_2O)(CH_3CO_2)$

What at first appeared to be well-shaped purple needles were obtained from the preparation of this compound. Upon close examination under the stereoscopic microscope, it appeared that the crystals may not be single. Most of the crystals had step-shaped ends. Several crystals were mounted on the precession camera and were found not to be single crystals, having two or more vertical lines and double spots on the precession photographs. Finally a crystal was located which appeared to extinguish totally along the needle axis through the polarizing microscope and did not have visible step-shaped ends. This crystal was mounted on the precession camera and precession photographs were taken.

It was not apparent from these photographs that the crystal was not single. The photographs indicated a triclinic unit cell with the following unit cell parameters: a = 18.60(3)Å, b = 10.19(2)Å, c = 10.73(2)Å, α = 70.85(8)°, β = 69.90(8)°, γ = 26.00(8)° V = 387.7Å^3. The experimental density measured by Kalyanaraman (55), 1.68(1) g/cm^3, agrees well with the calculated density for two formula units per unit cell, 1.68 g/cm^3. The crystal was then mounted on the diffractometer and during attempts to align the crystal it was found that the crystal was not single. No intensity data were collected.

Crystallographic Data for $Mg(C_5H_7O_2)_2 \cdot 2H_2O$

A well-formed needle crystal with dimensions 0.12 x 0.09 x 0.89 mm was mounted on a glass rod. The crystal's long dimension, b, was mounted along the spindle axis of the precession camera. The crystal had a triangular shape when viewed from an end. Precession photographs were taken using nickel-filtered Cu Kα radiation, λ = 1.539Å. The crystal was found to be monoclinic with a = 10.97(2)Å, b = 5.35(1)Å, c = 11.14(2)Å, β = 106.48(9)° and V = 627.2Å^3. The systematic absence of the reflections with $l = 2n + 1$ on the $h0l$ zone and the systematic absence of the reflections with $k = 2n + 1$ on the $0k0$ line were consistent with the space group $P2_1/C$ (No. 14). The density calculated on the basis of two monomer units of $Mg(C_5H_7O_2)_2 \cdot 2H_2O$ per unit cell, 1.35 g/cm^3, agrees well with the experimental value, 1.35(1) g/cm^3, obtained by the flotation method using a mixture of methanol and carbon tetrachloride.

Since the space group is $P2_1/c$ and there are two molecules per

unit cell, the molecule must sit on an inversion center; all of the special positions in $P2_1/c$ are inversion centers. The molecule must be monomeric and have the trans configuration. Therefore, the magnesium(II) acetylacetonate dihydrate appears to be isostructural with nickel(II) acetylacetonate dihydrate (56) and with cobalt(II) acetylacetonate dihydrate (57), as can be seen from Table 11.

Table 11. Crystallographic Data for Metal Acetylacetonate Dihydrates

Metal	a,Å	b,Å	c,Å	β
Magnesium	10.97	5.35	11.14	106°29'
Cobalt	10.91	5.39	11.19	106°00'
Nickel	10.95	5.36	11.25	106°48'

Crystallographic Data for $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ (18)

A well-formed green needle-like crystal with approximate dimensions 0.1 x 0.1 x 0.6 mm was mounted on a glass rod with one of slanted end faces of the crystal perpendicular to the long axis of the rod. This was then mounted on the precession camera and orientation precession photographs were taken using zirconium-filtered Mo Kα radiation, λ = 0.7106Å. Viewed from the end the crystal is shaped like a triangle. The crystal was found to be monoclinic with a = 21.55(4)Å,

b = 10.88(2)Å, c = 20.00(4)Å, β = 121.4(1)° and V = 4002Å^3. The density calculated on the basis of four tetramer formula units per unit cell, 1.47 g/cm^3, agrees well with the experimental value, 1.47(1) g/cm^3, obtained by the flotation method using a mixture of benzene and methylene iodide. Comparison of the unit cell parameters and density with those of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ is of interest. For the cobalt complex a = 21.79(4)Å, b = 10.91(2)Å, c = 20.21(4)Å, β = 121.7(1)° and V = 4086Å^3. For the cobalt complex the calculated density is 1.43 g/cm^3, and the experimental density is 1.40 g/cm^3. All of the precession photographs of the nickel complex showed the same systematic absences as the cobalt complex. The absence of hkl reflections with $h + k = 2n + 1$ and the absence of $h0l$ reflections with $l = 2n + 1$ indicated space group Cc (No.9) or C2/c (No.15). Also, all nickel reflections on the $hk0$, $h0l$, $hk1$ and $h1l$ levels had the same relative intensities as the corresponding reflections from the cobalt crystal. Since the photographs are superimposable on one another, $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ is exactly isostructural with $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ for which the solution of the structure has already been discussed.

Crystallographic Data for $Ni(C_{10}H_{11}NO_2)(C_2H_5OH)$

These green crystals grow in plates and all of the crystals examined were found not to be single. Under the microscope the crystals appeared to be many thin plates stacked in such a way as to appear to be one thicker plate. Some crystals which appeared to be single under the microscope were found not to be single when precession photographs were

taken.

Crystallographic data for $Ni(C_{10}H_{11}NO_2)$

A well-formed red-brown crystal was mounted for space group work. Precession photographs were taken with zirconium-filtered molybdenum Kα radiation. Zero level and first level zone photographs were taken at three different spindle settings. Several additional zero level pictures were taken. A complete plot of reciprocal space was drawn. The zones were not 90 degrees apart, therefore the plot was not consistent with an orthorhombic space group. The absences found would be consistent with two glide planes, which cannot be present in a monoclinic unit cell. The reciprocal space plot did not appear to agree well with any space group, and work on this complex was set aside.

Crystallographic Data for $NiC_{10}H_{14}N_4O_4$

A red needle crystal with dimensions 0.13 x 0.13 x 1.14 mm was mounted on the precession camera with the long dimension along the spindle axis. Viewed from the end the crystal appears as a perfect square with all 90° angles. Orientation precession photographs were taken, using nickel-filtered Cu Kα radiation, $\lambda = 1.542$Å. The crystal was found to have a tetragonal unit cell with unit cell parameters determined from the precession photographs of $a = b = 14.31(2)$Å, $c = 6.60(1)$Å and V = 1352Å^3. The same crystal and goniometer used for space group determination were transferred to the automated Picker diffractometer. The diffractomer and crystal were aligned according to published instructions (52). The four angles (ϕ, χ, ω and 2θ) which define the position of the crystal and counter to record a reflection in

reciprocal space, were determined for 12 reflections. From these 12 reflections, refined unit cell parameters and angle settings for the remaining data were obtained by a least-squares method using the Carter computer program (53). The cell parameters obtained from the diffractometer data are $a = b = 14.315(2)$Å, $c = 6.602(1)$Å and $V = 1353$Å^3, using Mo Kα radiation, $\lambda = 0.7107$Å.

The calculated density of 1.54 g/cm^3 for four formula units of $NiC_{10}H_{14}N_4O_4$ per unit cell agrees well with the observed experimental density of 1.55(1) g/cm^3 measured by the flotation method using diiodomethane and chloroform.

The general absence of hkl reflections with $h + k + l = 2n + 1$ was consistent with the following space groups I422 (No. 97), I4mm (No. 107), $I\bar{4}m2$ (No. 119), $I\bar{4}2m$ (No. 121) and I4/mmm (No. 139). A complete set of data was collected on the diffractometer using the θ-2θ scan technique. A three-dimensional Patterson synthesis run with the above data was not consistent with any of these space groups. Refinement was tried with I422, but was not successful. In the collection of data many peaks appeared more split than usual. The crystal may have multiple crystal problems or disorder problems that contribute to the trouble in interpretation.

Crystallographic Data for $Ni(TEA)_2Cl_2$

A reasonably well-shaped blue crystal of $Ni(TEA)_2Cl_2$ with approximate dimensions 0.1 x 0.1 x 0.3 mm was mounted on the precession camera and precession photographs were taken using zirconium-filtered Mo Kα radiation. The crystal was found to be triclinic. The crystal

was then transferred to the Picker automated diffractometer. Twenty-three top-to-bottom and left-to-right centered reflections were used as input for the Carter program (53) in aligning the diffractometer. The values of the parameters and errors calculated by Carter's program were a = 9.034(2)Å, b = 7.397(1)Å, c = 4.467(1)Å, α = 83.28(2)°, β = 70.32(1)°, γ = 76.85(1)° and V = 447Å^3. The density calculated on the basis of one formula unit of $Ni(TEA)_2C\ell_2$ per unit cell, 1.60 g/cm^3, agrees well with the experimental value, 1.60(1) g/cm^3, obtained by the flotation method using carbon tetrachloride. A complete set of intensity data was not collected due to a nonsingle crystal problem.

Analyses

All carbon, hydrogen and nitrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

A modification of the procedure of Kolthoff and Sandell (58) was used for the nickel analysis of $Ni(C_{10}H_{11}NO_2)$. The red crystals were dissolved with a mixture of hydrogen peroxide, perchloric acid and sulfuric acid. The complex dissolved forming a green solution. When the solution was cooled to dry ice temperature, long yellow needles formed from the solution. Ammonium hydroxide was added until basic and, when the mixture was heated everything went into solution. The solution was then placed into position for an electrodeposition with a platinum cathode and a platinum anode. Ammonium hydroxide was added periodically during the electrolysis to prevent any precipitation. The electrodeposition was conducted between three and four volts. In two hours all of the nickel had plated out. This was shown by lowering the cathode

and after ten minutes no additional nickel plated on the upper nickel-free portion.

Magnetic Studies

Magnetic measurements were made either by the Faraday method or the Gouy method. A computer program written by Bertrand was used to calculate the results. The gram susceptibility, χ_g, has been corrected for the susceptibilities of the sample tube and the displaced air. The molar susceptibility, χ_m, has been corrected for the diamagnetism of the atoms using the diamagnetic corrections of Figgis and Lewis (59). The magnetic moments, μ, were calculated using the equation

$$\mu = 2.84(\chi_m T)^{\frac{1}{2}}$$

where T is the absolute temperature.

Magnetic Moment of $[Cu(C_8H_{10}N_2O)]_2$

In the Faraday method (59) the force developed by a small sample suspended in a magnetic field of constant dH/dx is measured. The field was developed using an Alpha Scientific Laboratories Model 40-50A current regulated power supply coupled to an Alpha Model 9500 Electromagnet fitted with Heyding pole tips. Force on the sample was measured using a Cahn R. G. Automatic Electrobalance coupled to a Minneapolis-Honeywell galvanometer (sensitivity equal to 0.006 μa/mm). The small glass holder was suspended by a very fine braided nylon thread. The measurement was determined at 26.5°C using $HgCo(CNS)_4$ as a calibrant with the value (59) of 16.44×10^{-6} for the susceptibility. The values obtained for

$[Cu(C_8H_{10}N_2O)]_2$ were: $\chi_g = 1.7(5) \times 10^{-7}$, $\chi_m^{corr} = 1.2(1) \times 10^{-4}$, and $\mu_{eff} = 0.54(2)$ B.M. The deviation shown reflects the deviation of values obtained in measurements made at six field strengths.

Magnetic Moment of $Co_2(C_4H_{10}N_2O)_3(OCH_3)I$

This magnetic measurement was made at room temperature (302.00°K) by the Gouy method as previously described (60). The molecular weight used in the calculation was 588.193. The values obtained for $[Co_2(C_4H_{10}N_2O)_3(OCH_3)I]$ were: $\chi_g = 13.5(2) \times 10^{-6}$, $\chi_m^{corr} = 8.0 \times 10^{-3}$, and $\mu_{eff} = 4.38(2)$ B.M. per dimer. The deviation shown reflects the deviation of values obtained in measurements made at eight field strengths.

CHAPTER III

RESULTS AND DISCUSSION

Structure of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ (Q)

A perspective drawing of the structure prepared by C. K. Johnson's program, ORTEP (50), is shown in Figure 1. R1 and R2 on the figure denote chelate rings one and two; the R1 and R2 designations are not repeated at the atoms of the rings. Table 12 presents selected intramolecular distances and angles. Table 13 lists selected dihedral angles between planes within the molecule. The structure consists of discrete tetramers similar to those reported for Tetra-μ_3-methoxytetrakis[salicylaldehydato(ethanol)nickel(II)] (19). Four cobalt atoms and four methoxide oxygen atoms form a cubane-type unit which consists of two interpenetrating tetrahedra. One of the tetrahedra is formed by the cobalt atoms and the cobalt-to-cobalt distance varies from 3.10Å to 3.17Å as given in Table 12. The other tetrahedron is formed by the four methoxide oxygen atoms. There is a cobalt-oxygen bond along every edge of the cube of the cubane-type structure; the cobalt-oxygen distances along these edges vary from 2.04Å to 2.14Å. Each methoxide group bridges three cobalt atoms with Co-O-Co angles of 94.6° to 98.4°.

Slightly distorted octahedral coordination of each cobalt atoms is completed by a chelated acetylacetonate group and a coordinated methanol molecule. The ring formed by the cobalt atoms and the chelated

acetylacetonate group is essentially planar as shown by the dihedral angles in Table 13. Bond angles at cobalt vary from 81° to 100°; the cobalt to acetylacetonate oxygen bond distance varies from 2.00Å to 2.05Å. The coordinated methanols give the longest Co-O distances, 2.15Å and 2.20Å. The chelate rings and the methanols are related in pairs by a twofold axis through the center of the molecule, parallel to y, with coordinates of $x = 0$ and $z = 1/4$. Although this twofold axis is the only crystallographically required site symmetry, the molecule also has an approximate fourfold inversion axis. Although the top four-membered ring of the cubane, Co1-O1-Co1'-O1', has long (2.11Å) and short (2.06Å) bonds and the bottom four-membered ring, Co2-O2-Co2'-O2', has long (2.14Å) and short (2.04Å) bonds, the long bonds are immediately under one another and the short bonds are immediately under one another and not rotated by 90° as they would be for a true fourfold inversion axis.

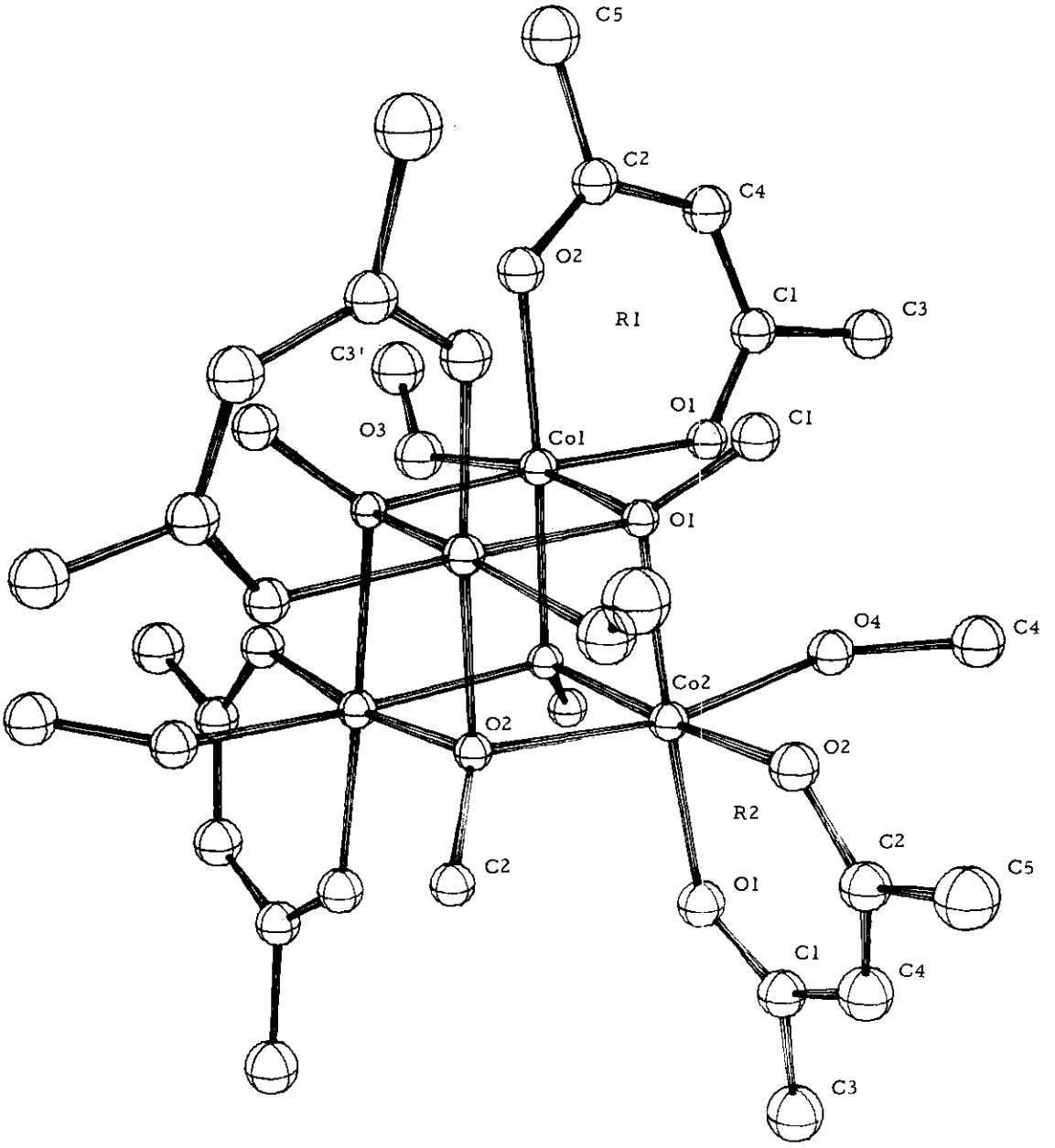


Figure 1. A Perspective Drawing of the Structure of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$

Table 12. Selected Intramolecular Distances and Angles in $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$

Atoms	Distance, Å	Atoms	Angle, degrees
Co1-Co1'*	3.16(1)	Co1-O1-Co1'	98.4(6)
Co1-Co2	3.10(1)	Co2-O2-Co2'	98.6(5)
Co1-Co2'	3.12(1)	Co1-O1-Co2	94.6(5)
Co2-Co2'	3.17(1)	Co2-O1-Co1'	97.0(5)
Co1-O1	2.11(1)	Co1-O2'-Co2	98.3(5)
Co1-O1'	2.06(1)	Co1-O2'-Co2'	95.8(5)
Co1-O2'	2.06(1)	O1-Co1-O1'	81.5(6)
Co2-O2	2.04(1)	O1-Co1-O2'	82.5(5)
Co2-O2'	2.14(1)	O1'-Co1-O2'	84.5(5)
Co2-O1	2.11(1)	O1-Co1-R101	93.5(6)
Co1-O3	2.15(2)	O1-Co1-R102	100.4(6)
Co2-O4	2.20(2)	O1'-Co1-O3	88.9(6)
Co1-R101	2.05(1)	O3-Co1-R101	95.5(6)
Co1-R102	2.01(2)	O3-Co1-R102	89.1(7)
Co2-R201	2.00(2)	R101-Co1-R102	89.9(6)
Co2-R202	2.05(2)	O2-Co2-O2'	81.0(5)
O1-C1	1.41(3)	O2-Co2-O1	83.3(5)
O2-C2	1.46(2)	O2'-Co2-O1	81.5(5)
O3-C3'	1.38(4)	O2'-Co2-R201	100.3(6)
O4-C4	1.49(3)	O2-Co2-R201	97.6(6)

Table 12. (Continued)

Atom	Distance, Å	Atoms	Angle, degrees
R101-R1C1	1.30(3)	O2'-Co2-O4	86.9(5)
R1C1-R1C4	1.39(3)	O4-Co2-R201	88.4(6)
R1C2-R1C4	1.43(3)	O4-Co2-R202	96.5(6)
R102-R1C2	1.30(2)	R201-Co2-R202	89.8(7)
R1C1-R1C3	1.50(3)	Chelate Ring 1	
R1C2-R1C5	1.54(4)	Co1-R101-R1C1	127(1)
R201-R2C1	1.26(3)	R101-R1C1-R1C3	118(2)
R2C1-R2C4	1.43(3)	R101-R1C1-R1C4	125(2)
R2C2-R2C4	1.36(3)	R1C3-R1C1-R1C4	117(2)
R202-R2C2	1.30(3)	R1C1-R1C4-R1C2	125(2)
R2C1-R2C3	1.56(4)	R1C4-R1C2-R1C5	120(2)
R2C2-R2C5	1.55(3)	R1C4-R1C2-R102	125(2)
		R1C5-R1C2-R102	115(2)
		R1C2-R102-Co1	127(1)
		Chelate Ring 2	
		Co2-R201-R2C1	128(2)
		R201-R2C1-R2C3	115(2)
		R201-R2C1-R2C4	125(3)
		R2C3-R2C1-R2C4	119(2)

Table 12. (Continued)

Atoms	Angle, degrees
R2C1-R2C4-R2C2	124(3)
R2C4-R2C2-R2C5	119(3)
R2C4-R2C2-R202	128(2)
R2C5-R2C2-R202	113(2)
R2C2-R202-Co2	124(1)

* The ' indicates a twofold rotation parallel to y, with coordinates of $x = 0$ and $z = \frac{1}{4}$.

Table 13. Dihedral Angles Between Planes Each Defined by Three Atoms for $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$

Atoms of First Plane	Atoms of Second Plane	Angle, degrees
R1C1-R1C4-R1C2	R1O1-Co1-R1O2	5(2)
R1C1-R1C4-R1C2	R1C3-R1C1-R1C4	2(2)
R1C1-R1C4-R1C2	R1C4-R1C2-R1C5	0.1(24)
R2C1-R2C4-R2C2	R2O1-Co2-R2O2	6(3)
R2C1-R2C4-R2C2	R2C3-R2C1-R2C4	0.2(24)
R2C1-R2C4-R2C2	R2C4-R2C2-R2C5	3(2)
O1-Co-O1'*	O1-Co'-O1'	5(1)
O2-Co2-O2'	O2'-Co2'-O2	8(1)

* The ' indicates a twofold rotation parallel to y, with coordinates of $x = 0$ and $z = \frac{1}{4}$.

In order to study the effect of varying the metal ion in this cubane-type of complex, cubane complexes of this type have been examined with cobalt, nickel and magnesium. In line with this same objective crystals of the nickel complex, $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$, were prepared that were suitable for single crystal X-ray investigation; this nickel complex was found to be completely isostructural with the cobalt cubane complex for which the structure has been discussed. Of these three cubane complexes (28,38) the magnesium complex is diamagnetic; the room temperature magnetic moment of cobalt, 5.1 B.M., is normal for a high-spin octahedral Co(II), 4.7 B.M.-5.2 B.M.; and the room temperature magnetic moment of the nickel cubane complex, 3.3 B.M., is consistent with octahedrally coordinated Ni(II), 2.9 B.M.-3.4 B.M. In conjunction with the structure work on the cobalt and nickel complexes, a complete low temperature magnetic investigation of the nickel complex has been carried out at Bell Telephone Laboratories (28).

Since all the nickel atoms appear to be in an orbitally nondegenerate ground state, the tetrameric cluster provides an interesting opportunity to study spin-spin interactions in a crystal lattice composed of Ni_4 tetrahedra which are magnetically isolated from neighboring clusters by the peripheral ligands. The magnetic susceptibility of the nickel complex has been measured from 296°K down to 1.63°K, and the field dependence of the susceptibility has been examined up to 15.3 kilo-oersteds (kOe) at several temperatures below 20°K. Below 13°K, the susceptibilities measured were field dependent.

Starting from the room temperature magnetic moment of 3.31 B.M. per nickel atom, μ_{eff} increases steadily, showing an inflection between 10°K and 25°K, and has a value of 4.86 B.M. at 21°K. At even lower temperatures μ_{eff} continues to increase, reaching 5.80 B.M. at 1.63°K. The results demonstrate that the eight e_g electrons centered on the tetrad of nickel atoms are ferromagnetically coupled, the ground molecular spin state for the tetramer being S' = 4 (eight spins parallel) and being fully populated at 21°K. The magnitude of the intramolecular Ni-Ni coupling constant is J = +10°(or 7 cm^{-1}). The tetramer molecules in their ground state exhibit an additional intermolecular ferromagnetic coupling which gives rise to a Weiss constant θ = +0.8°. This complex provides the second example of a polynuclear ferromagnet in which the level of maximum spin multiplicity has been fully populated by taking it to very low temperatures; the first was $Ni_3(C_5H_7O_2)_6$ (61). It is the first example of a cluster complex found to exhibit both intramolecular and intermolecular ferromagnetic spin coupling. The complex $Ni_3(C_5H_7O_2)_6$ also shows interactions between the cluster units, but in this case the interaction is antiferromagnetic; the first observation of ferromagnetic exchange in a discrete, polynuclear cluster was in this trimer (61,62). After this work was in progress, Andrew and Blake published the structure of another cubane, $[Ni(sal)(OCH_3)(C_2H_5OH)]_4$ (19); it is very similar to the cubane structures discussed here.

Structure of $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$

It should be possible to prepare several geometric isomeric forms

of these cubane complexes, and this should lead to a better understanding of the relationship between isomeric polynuclear species which differ only in the relative positions of chelate groups on metal ions. Figure 2 where the cubane unit is viewed from the top of the cube shows six different geometric isomeric forms. It was thought that by varying reaction conditions and recrystallization techniques, one or more different geometric isomers might be obtained in the solid state. Along this line it was assumed that different geometric forms might crystallize at different temperatures; N.M.R. evidence indicated that the magnesium cubane appeared to rearrange between isomeric forms at room temperature (17). Preparation of the cobalt cubane complex at 0°C yielded tetragonal crystals of $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$ of space group $I\bar{4}2m$ (No. 121), with two tetramers per unit cell. $I\bar{4}2m$ was chosen as the most probable space group since the other space groups consistent with the diffraction symmetry would require the molecule to have fourfold symmetry. The molecule is, thus, required to occupy a site of $\bar{4}2m$ symmetry and this structure labelled $\bar{4}m$ in Figure 2 appeared to be the only reasonable possibility; as will be explained the structure was disordered in such a way that molecules of a different symmetry could occupy these sites.

The acetylacetonate rings and the water molecules are disordered in this structure. Two ORTEP perspective drawings, Figure 3 and Figure 4, are included for this molecule in order to illustrate the disorder present. Table 14 presents selected intramolecular distances and angles; Table 15 lists selected dihedral angles between planes within

the molecule. In order to apply the labelling system used to name a particular atom in the figures and tables, it is necessary to apply the following numbered symmetry operations: basic, x,y,z; no. 1, twofold rotation, $\bar{x},\bar{y},z$; no. 2, twofold rotation, $\bar{x},y,\bar{z}$; no. 3, twofold rotation, $x,\bar{y},\bar{z}$; no. 4, fourfold inversion, $\bar{y},x,\bar{z}$; no. 5, fourfold inversion, $y,\bar{x},\bar{z}$; no. 6, mirror, y,x,z; no. 7, twofold rotation and mirror, $\bar{y},\bar{x},z$. As an illustrative example 01,6 is used to represent an atom at coordinates -- 0.0752, 0.2378, 0.0824 -- while 01 represents an atom located at coordinates -- 0.2378, 0.0752, 0.0824.

The structure consists of discrete tetramers very similar to those previously discussed for $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$. Four cobalt atoms and four methoxide oxygen atoms form a cubane-type structure; and this basic cubane-type unit, $Co(OCH_3)_4$, is not affected by the disorder within the structure. All of the atoms of the acetylacetonate ligand with the exception of 09 which lies on the mirror plane (01, C2, C3, C4, C5 and C6) are disordered. It was necessary to put these atoms into the structure factor calculation in general positions, Wykoff 16j sets, with multipliers of 0.5 in order to place half of the electron density in each of the disordered positions. An attempt has been made in Figure 3 and Figure 4 to demonstrate one form this molecular disorder can take. In the first drawing, Figure 3, the forward-and-upper acetylacetonate ring lies generally to the left in an x,y,z type position. Other acetylacetonate rings in this structure are related to this ring by symmetry operations no. 1, no. 4 and no. 5. In the second drawing, Figure 4, the cubane type unit, $Co_4(OCH_3)_4$, remains the same as before.

The forward and upper acetylacetonate ring has been reflected to a position on the right which is a mirror image of the original position. The ring positions in this second drawing are related to the original x,y,z position by the following symmetry operations: no. 2, no. 3, no. 6 and no. 7. Close inspection will show that the structure in the second drawing is a different orientation of the structure in the first drawing. If the molecules in the structure would alternate between the orientation in the first drawing and the orientation in the second drawing, this would be one possible way of achieving the overall observed disorder present. However, the observed overall disorder can be achieved by any method which places half of the electron density in each of the disordered positions; for example, different isomers could randomly occupy the molecular sites. There appears to be no way in which to make a distinction between the above possibilities. Unlike the structure of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$, where the terminal position on each cobalt is a methanol molecule, in $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$ the terminal position is a water molecule.

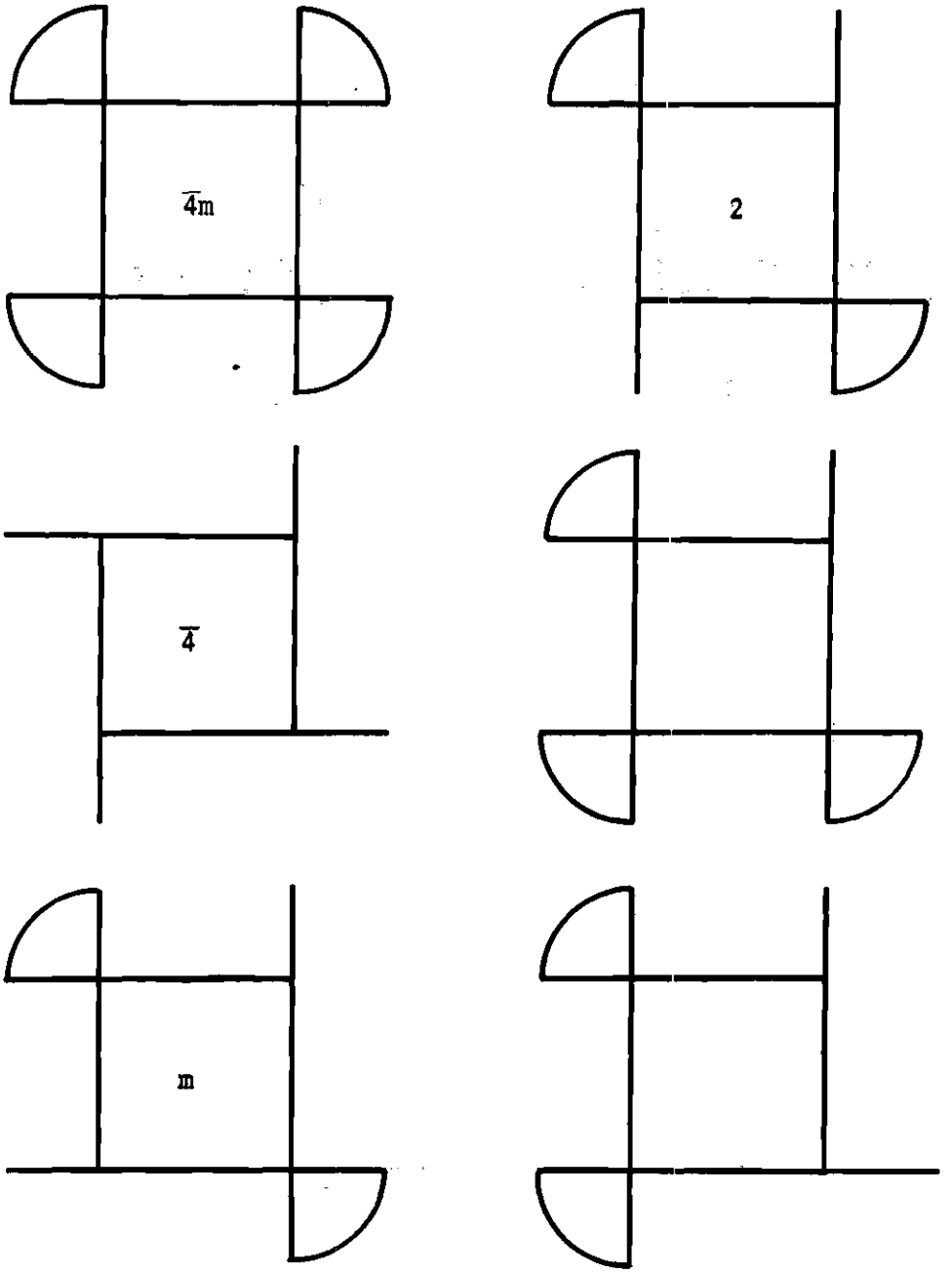


Figure 2. Different Geometric Isomeric Forms for the Methoxide-Acetylacetonate Cubane Complexes

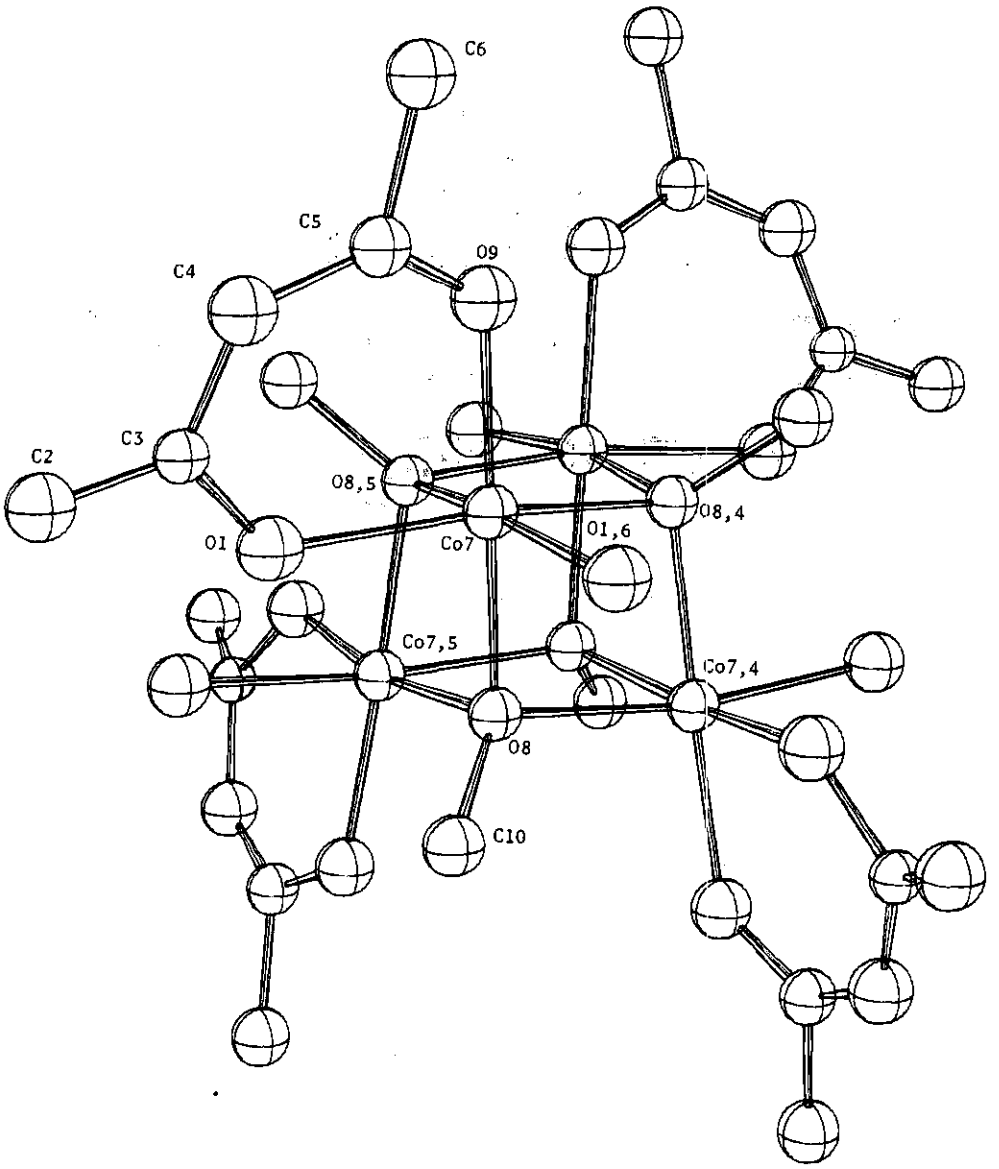


Figure 3. First Perspective Drawing of the Structure of $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$

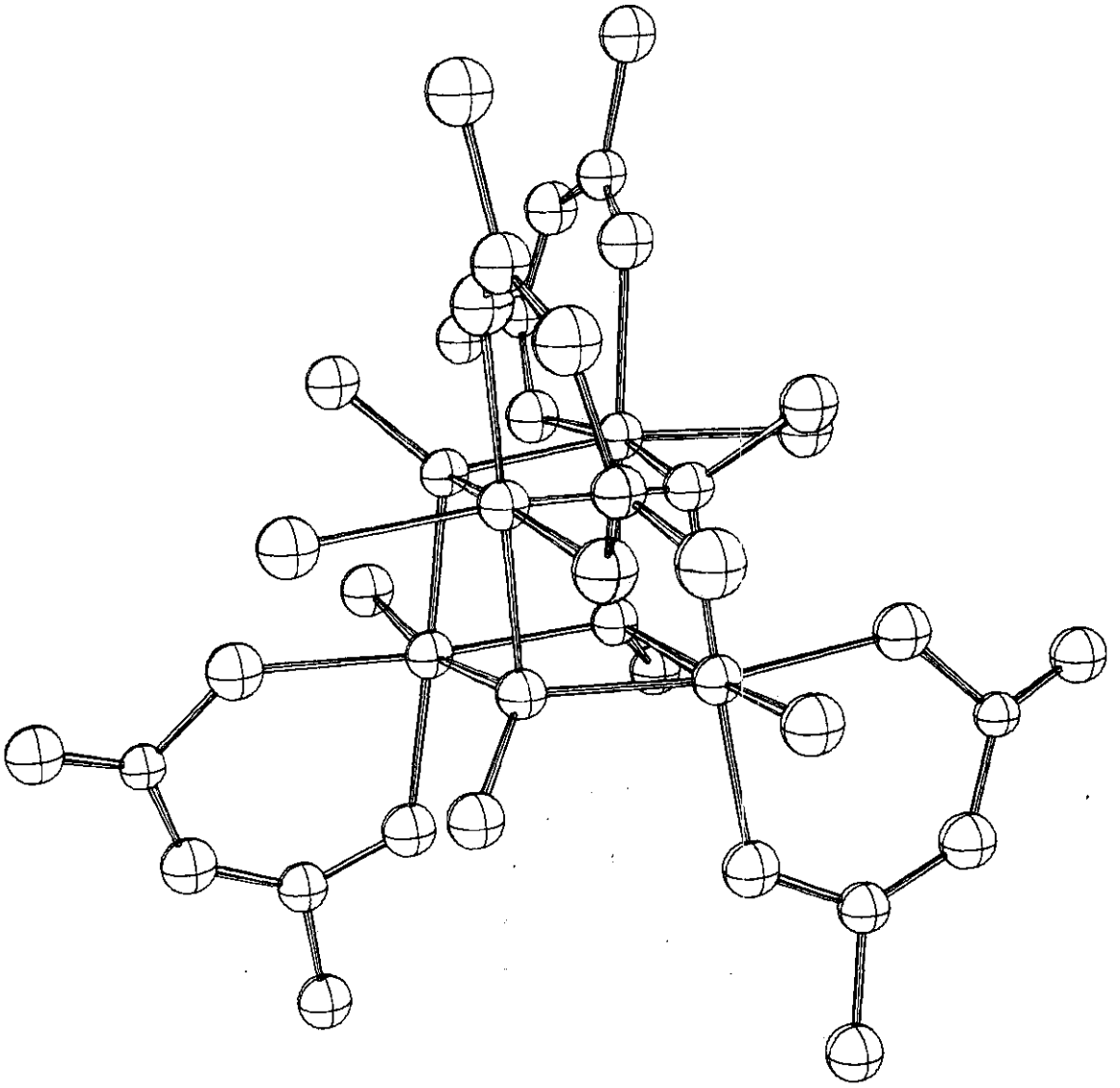


Figure 4. Second Perspective Drawing of the Structure of $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$

Table 14. Interatomic Distances and Angles for $[Co(C_5H_7O_2)(CH_3O)(H_2O)]_4$

Atoms	Distance, A	Atoms	Angle, degrees
Co7-O1	2.17(2)	O1,6-Co7-O1	94.7(11)
Co7-O8,5	2.08(3)	O1-Co7-O8,5	93.1(6)
Co7-O8,4	2.08(1)	O8,5-Co7-O8,4	78.0(8)
Co7-O1,6	2.17(2)	O8-Co7-O1	91.4(10)
Co7-O9	2.04(2)	O1-Co7-O9	89.0(11)
Co7-O8	2.03(2)	O8-Co7-O8,5	80.2(6)
O8-Co7,5	2.08(1)	O8,5-Co7-O9	99.3(5)
O8-Co7,4	2.08(3)	C10-O8-Co7,5	118.3(14)
O8-C10	1.52(4)	Co7,5-O8-Co7	98.5(6)
O9-C5	1.34(5)	Co7,5-O8-Co7,4	101.6(8)
O1-C3	1.40(4)	Co7-O8-C11	117.8(17)
C2-C3	1.28(6)	Co7-O9-C5	120.8(29)
C3-C4	1.37(6)	O9-C5-C6	105.1(60)
C4-C5	1.35(7)	C6-C5-C4	122.4(64)
C5-C6	1.55(8)	C4-C5-O9	132.0(49)
		C5-C4-C3	131.1(58)
		O1-C3-C4	116.7(42)
		C4-C3-C2	130.3(52)
		C2-C3-O1	110.9(41)
		C3-O1-Co7	128.1(20)

Table 15. Dihedral Angles Between Planes Each Defined by Three Atoms for $[Co(C_5H_7O_2)(CH_3O)(H_2O)]_4$

Atoms of First Plane	Atoms of Second Plane	Angle, degrees
O1-Co7-O9	O1-C4-O9	170.9(22)
O1-C4-O9	C4-C4-O9	7.1(68)
O1-C4-O9	O1-C3-C4	0.6(53)
C4-C5-C6	C4-C5-O9	171.8(106)
C2-C3-C4	O1-C3-C4	161.9(96)

An attempt was made to vary the alkyl groups on the alcohols and alkoxide groups of these complexes; in this way the steric requirements imposed on the complex could be changed. The terminal alcohols of the nickel cubane complex can be exchanged at will by boiling the complex in another alcohol such as ethanol or isopropanol, but the μ_3-methoxide bridges of the cubane are not affected; it appears that the cubane unit remains intact throughout the exchange reactions. These cubanes have been found to retain their tetrameric character in a chloroform solution at 37°C (38). Recent work (20) has shown that the magnesium cubane complex disproportionates in dichloromethane to give magnesium(II) methoxide and magnesium(II) acetylacetonate dihydrate. The latter compound was investigated and found to be isostructural with nickel(II) acetylacetonate dihydrate and cobalt(II) acetylacetonate dihydrate; the compound was found to be an octahedral magnesium complex with trans water molecules.

By heating the cubanes in vacuum at 100°C the alcohol was removed. Molecular weight studies (38) indicate that the same type of cluster is present after removal of the methanol; and the metal ions are, thus, five coordinate.

A cubane unit similar to these methoxide cubane units can be obtained through the use of Schiff's bases as ligands with copper and cobalt.

When EIA was used as the ligand, Co(II) and Cu(II) gave tetrameric cubane complexes (36); in these complexes the metal is five coordinate as in the alcohol-free alkoxide cubane complexes. The

complete single crystal X-ray structure of $[Cu(EIA)]_4$ has been determined (63) and $[Co(EIA)]_4$, prepared and investigated in this work, has been found to be isostructural with $[Cu(EIA)]_4$ by the use of X-ray powder diffraction photograph comparisons.

In these complexes the bridging oxygen is tetrahedrally coordinated. These tetrameric complexes, like the previously reported acetylacetone-mono-(o-hydroxyanil)-copper(II) (24), can be thought of as two dimers held together by Co-O bonds. In the previous structure, one dimer was displaced with respect to the other so that there were only two such interactions per tetramer; in the ethanolimine complex, one dimer is rotated 90° with respect to the other so that there are four Co-O interactions. In the isostructural copper complex the metal-metal distance is 3.26Å. The molecule sits on a twofold site symmetry axis and the four-membered metal-oxygen ring is thus not required to be planar. In the isostructural copper complex the extent of bending of this ring is indicated by the dihedral angles between the two M-O-M planes, 14°, and between the two O-M-O planes, 12°. The carbon bonded to the bridging oxygen also shows the effect of bending the ring.

The $[Cu(PIA)]_2$ complex formed a dimer with a planar four-membered metal-oxygen ring. Although their formulas differ by only one carbon atom, the room temperature magnetic moments of $[Cu(PIA)]_2$ and $[Cu(EIA)]_4$ are markedly different, 0.41 B.M. and 1.87 B.M., respectively. In the case of $[Cu(PIA)]_2$, it is possible to have M-O-C angles of 129° and square-planar coordination around copper without any steric strain;

however, the same arrangement in the M(EIA) complexes, because of the smaller chelate ring, would be extremely strained. The strain can be relieved to some extent by a change to sp^3 hybridization of the oxygen orbitals, thus decreasing the M-O-C angle within the chelate ring; this angle is 108° in Cu(EIA).

With the change in hybridization of the oxygen, the ethanolimine ligand makes it impossible to have a planar four-membered metal-oxygen ring and square-planar coordination of the metal; in the cobalt and copper tetramers the four-membered ring is slightly bent and the metals are five coordinate.

Structure of $[Ni(EIA)]_2$

Recently EIA was reacted with nickel(II) acetate (40); a complex with the empirical formula $Ni(EIA)(CH_3OH)$ was isolated. The green, paramagnetic compound lost methanol readily in a stream of inert gas and the resulting red compound, $[Ni(EIA)]_2$, was diamagnetic. A comparison of the properties of the methanolate to those of $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ suggested a similar cubane type structure; however, the methoxide compound required more severe conditions to remove the methanol and the resulting green compound was paramagnetic. To obtain more information about the coordination of nickel and the association into polymeric units, structure determinations were initiated; the description of the structure of the red, diamagnetic compound, $[Ni(EIA)]_2$, is reported here.

Figure 5 shows an ORTEP perspective drawing of the structure. Table 16 presents selected intramolecular distances and angles. The

structure consists of discrete dimers; a twofold axis relates the two halves of each dimer. The four-membered ring of nickel and oxygen is distinctly bent; the dihedral angle between the two Ni-O-Ni planes of the ring is 43°, and the dihedral angle, Table 17, between the O-Ni-O planes of the ring is 39°. The coordination around the nickel is essentially planar; for the nickel and the four atoms coordinated to it, the greatest distance of any atom from the least-squares plane consisting of these five atoms is 0.01Å. Equations of least-squares atomic planes and the distances of atoms from these planes (3) are given in Table 18. The bond angles at nickel vary from 80.4° for the O-Ni-O angle of the four-membered ring to 96.9° for the O-Ni-N angle of the six-membered ring. The O-Ni-N angle in the five-membered chelate ring is 88.8° and the noncyclic O-Ni-O angle is 94.0°. The Ni-O bond lengths are 1.81Å for the oxygen of the six-membered ring, 1.85Å for the oxygen common to the four-membered and five-membered rings and 1.88Å for the oxygen of the four-membered ring; the Ni-N distance is 1.85Å. The molecules are packed together in such a way that the closest intermolecular approach to the nickel atom is by a methyl group, 3.9Å.

The coordination around the bridging oxygen is pyramidal with bond angles of 92.2°, 108.5° and 122.8°; dihedral angles between the Ni-O-Ni plane and the two Ni-O-C planes are 54° (for the nickel within the same five-membered chelate ring) and 66°.

The carbons within the six-membered ring and the methyl carbons of the six-membered ring are essentially planar with none of the atoms deviating more than 0.02Å from their least-squares plane, Table 18; the

dihedral angle between the carbon plane and the O-Ni-N plane of the same chelate rings is only 2°. Although there is a difference (1.44Å, 1.36Å) between the two C-C bond distances within the six-membered chelate ring, both distances are considerably less than the normal C-C single-bond distance (1.54Å). As a further indication of delocalization within the ring, the C-O (1.29Å) and C-N (1.28Å) distances of this ring are significantly shorter than the C-O (1.46Å) and C-N (1.50Å) distances of the five-membered ring.

Although hydrogen atoms were not refined, the observed positions of the hydrogens on the five-membered ring indicate that the hydrogens are staggered by about 30°.

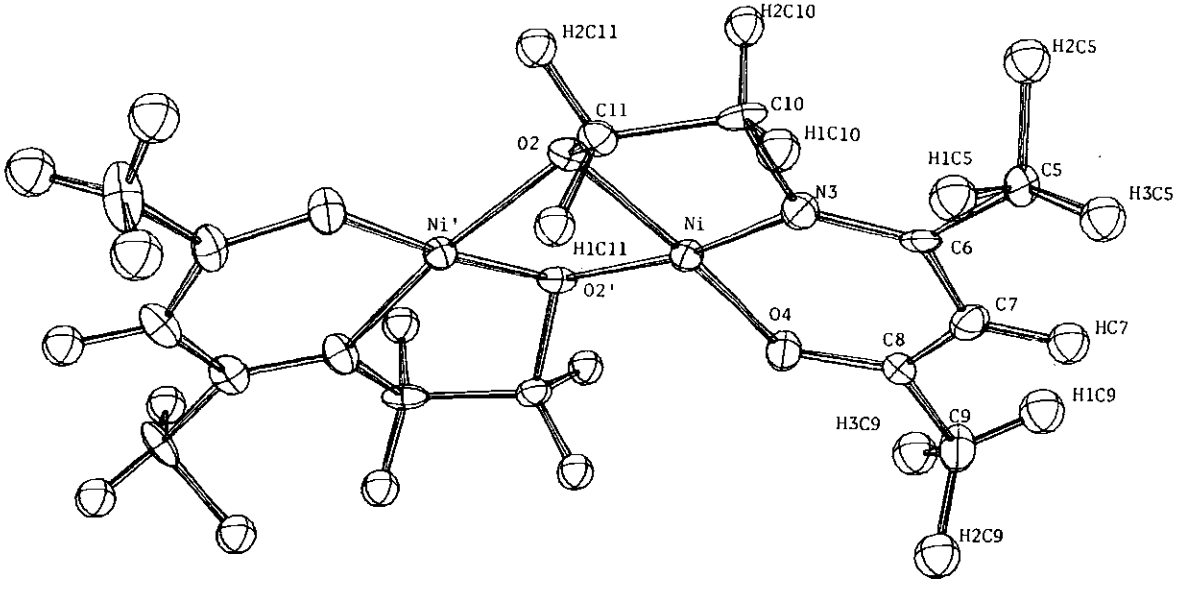


Figure 5. A Perspective Drawing of the Structure of $[Ni(EIA)]_2$

Table 16. Interatomic Distances and Angles for $[Ni(EIA)]_2$

Atoms	Distance, Å	Atoms	Angle, degrees
Ni1-Ni1'	2.690(4)	Ni1-O2-Ni1'	92.2(2)
Ni1-O2	1.849(6)	O2-Ni1-O2'	80.4(3)
Ni1-O2'	1.884(6)	O2-Ni1-N3	88.8(3)
Ni1-N3	1.849(7)	O2'-Ni1-O4	94.0(3)
Ni1-O4	1.812(6)	N3-Ni1-O4	96.9(3)
O2-C11	1.464(8)	Ni1-O2-C11	108.5(4)
O4-C8	1.288(9)	Ni1'-O2-C11	122.8(4)
N3-C6	1.276(9)	N3-C10-C11	107.7(7)
N3-C10	1.50(1)	O2-C11-C10	106.1(6)
C5-C6	1.50(1)	Ni1-N3-C10	110.3(6)
C6-C7	1.44(1)	C10-N3-C6	123.0(7)
C7-C8	1.36(1)	Ni1-N3-C6	126.4(6)
C8-C9	1.52(1)	N3-C6-C7	121.5(8)
C10-C11	1.50(1)	C6-C7-C8	124.5(8)
C5-H1C5	1.37	C7-C8-O4	125.6(8)
C5-H2C5	1.25	Ni1-O4-C8	124.8(5)
C5-H3C5	0.95	O4-C8-C9	114.3(8)
C7-HC7	1.06	C7-C8-C9	120.1(9)
C9-H1C9	1.06	N3-C6-C5	121.9(8)
C9-H2C9	1.24	C5-C6-C7	116.6(8)

Table 16. (Continued)

Atoms	Distance, Å	Atoms	Angle, degrees
C9-H3C9	0.95	H3C9-C9-C8	115.8
C10-H1C10	1.09	H3C9-C9-H1C9	107.1
C10-H2C10	1.08	H3C9-C9-H2C9	86.0
C11-H1C11	1.16	H2C9-C9-C8	114.4
C11-H2C11	1.12	H1C9-C9-C8	107.1
		H1C9-C9-H2C9	124.9
		HC7-C7-C8	117.5
		HC7-C7-C6	117.9
		H1C5-C5-C6	100.4
		H1C5-C5-H3C5	90.0
		H1C5-C5-H2C5	94.9
		C6-C5-H3C5	134.8
		C6-C5-H2C5	115.3
		H2C5-C5-H3C5	107.3
		H1C10-C10-N3	103.2
		H1C10-C10-H2C10	135.0
		H1C10-C10-C11	107.3
		N3-C10-H2C10	103.7
		H2C10-C10-C11	98.0
		H1C11-C11-C10	116.7

Table 16. (Continued)

Atoms	Angle, degrees
H1C11-C11-H2C11	112.5
H2C11-C11-O2	92.1
H1C11-C11-O2	110.8
H2C11-C11-C10	115.3

Table 17. Dihedral Angles Between Planes Each Defined by Three Atoms for $[Ni(EIA)]_2$

Atoms of First Plane	Atoms of Second Plane	Angle, degrees
Ni-O2-Ni1'	Ni-C11-O2	54.3(5)
Ni1-O2-Ni1'	Ni1'-O2-C11	66.2(6)
Ni1-N3-O4	C6-C7-C8	2.5(12)
Ni1-O2-Ni1'	Ni1-O2'-Ni1'	43.0(4)
O2-Ni1-O2'	O2-Ni1'-O2'	38.8(4)
O2'-Ni1-O2	Ni1-N3-O4	178.3(2)
Ni1-O2'-O4	Ni1-N3-O2	1.7(2)
O2'-Ni1-O2	Ni1-O2'-O4	179.7(3)
Ni1-N3-O4	Ni1-N3-O2	178.4(3)
Ni1-N3-O2	O2-Ni1-O2	0.6(3)

Table 18. Equations of Least-Squares Atomic Planes and Distances of Atoms (A) from these Planes for $[Ni(EIA)]_2$

(a) Equation of the Least-Squares Plane of the Coordination Sphere (Ni1,O2,O2',N3,O4):

$$0.253X + 0.947Y - 0.197Z = 2.030$$

Atom	Distance from Plane, A
Ni1	-0.001
O2	-0.014
O2'	0.015
N3	0.014
O4	-0.014

(b) Equations of the Least-Squares Plane of the Six-membered Ring Carbon Atoms (C5,C6,C7,C8,C9):

$$0.190X + 0.971Y - 0.145Z = 2.036$$

Atom	Distance from Plane, A
C5	-0.010
C6	0.004
C7	0.017
C8	-0.006
C9	-0.005

Table 18. (Continued)

(c) Equations of the Least-Squares Plane the Following Atoms (C5,C6,C7,C8,C9,O4,N3):

$$0.205X + .966Y - .159Z = 1.998$$

Atom	Distance from Plane, A
C5	-0.022
C6	0.013
C7	0.015
C8	0.007
C9	-0.006
O4	-0.016
N3	0.009

This $[Ni(EIA)]_2$ structure is very similar to that found (41) for the d^8 rhodium(I) dimer, $[Rh(CO)_2C\ell]_2$; the rhodium complex has a dihedral angle of 56° between the two Cℓ-Rh-Cℓ planes while $[Ni(EIA)]_2$ has a dihedral angle of 39° between the two O-Ni-O planes. Both complexes have planar coordination about the metal and both are diamagnetic. The cause of the dihedral angle in the nickel dimer appears to be related to the steric limitations of the ligand; however, no analogous steric limitations are present in the complex of rhodium (41). As suggested for the rhodium dimer, the dihedral angle may be related to direct metal-metal interactions; however, the nickel-nickel distance, 2.69Å, is greater than that in nickel metal, 2.50Å, or that in nickel arsenide, 2.52Å.

This $[Ni(EIA)]_2$ structure is distinctly different from that found for the copper(II) complex of the Schiff's base formed from acetylacetone and 3-amino-1-propanol, $[Cu(PIA)]_2$. Although dimeric, $[Cu(PIA)]_2$ contains a four-membered copper-oxygen ring which is completely planar and the coordination around the bridging oxygens is completely planar; π-bonding, involving the copper d_{xz}, d_{yz} orbitals and the oxygen p_z orbitals, appears to be important in $[Cu(PIA)]_2$. Nickel(II), with one less electron per metal, would be expected to show even stronger π-bonding since the highest energy electrons in the copper structure are assumed to occupy π* orbitals. However, the steric limitations of the 2-aminoethanol ligand prevent such a planar arrangement; the Ni-O-C angle within the five-membered ring would have to be at least 120° to give a planar arrangement of Ni1, Ni1', and C11

about O2. The value found for the Ni1-O2-C11 angle, 109°, is indicative of sp^3 hybridization of the oxygen orbitals.

Even though sp^3 hybridization of the oxygen orbitals prevents planar coordination about the bridging oxygen, it should be possible for the metal-oxygen ring to be planar. In $[Ni(bdhe)]_2^{+2}$ (34), in which the coordination about nickels is trigonal-bipyramidal, the nickel-oxygen four-membered ring is planar; however, construction of a molecular model shows that, with EIA, square-planar coordination around nickel and a planar nickel-oxygen ring would create considerable strain within the chelate ring. For a square-planar d^8 system, there is a large ligand-field stabilization and the strain is relieved by bending the four-membered ring rather than altering the coordination.

As mentioned previously, in the corresponding copper(II) and cobalt(II) complex, the metal-oxygen four-membered ring shows much less bending than in the nickel compound; however, the coordination around the metal is no longer square-planar. The nitrogen has moved considerably out of the plane which includes the metal and the bridging oxygens. In addition two of the copper and cobalt *dimers* are joined by M-O bonds to form a cubane-type complex in which the metal is five coordinate.

The nature of the one-to-one adduct of Ni(EIA) and methanol is of considerable interest but the crystals are unstable and several attempts to collect diffraction data have been unsuccessful. The calculated weight loss for $Ni(EIA)(CH_3OH)$ losing methanol to go to Ni(EIA) is 13.8 per cent; the experimental weight loss upon drying the

green material in a vacuum at 100°C for several hours is 13.7 per cent. The Ni(EIA)(CH_3OH) complex changes to the red complex after a variable length of time when heated in the following solvents: carbon tetrachloride, 1,2-dibromomethane, toluene, nitromethane, benzene and acetylacetone. The green complex remains as a green solid when added to isopropyl alcohol. When the compound is dissolved in toluene and the temperature is raised above room temperature the solution gradually turns red-brown. In an attempt to add pyridine to the red dimer, the red complex was added to boiling pyridine and a red powder came out of solution. If a small amount of ethanol is added to a boiling m-xylene solution of the red complex, the solution immediately turns green.

The adduct could be formed by the addition of methanol perpendicular to the coordination plane of the nickel to give square-pyramidal coordination about nickel, retaining the dimeric structure; the coordination of methanol could also produce a dimer with trigonal-bipyramidal coordination about nickel, similar to $[Ni(bdhe)]_2^{+2}$. The relatively weak field associated with oxygen ligands could produce a high-spin five-coordinate complex consistent with observations. An alternative possibility would be the addition of methanol in the same way, accompanied by the association of dimers into tetramers with a cubane-type structure; this type of structure has been found, as described earlier, for $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$, for $[Cu(EIA)]_4$ and for $[Co(EIA)]_4$. The similarity of properties of $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ and the methoxide complex favor such a structure, but the ease with which the compound reversibly adds methanol

makes the tetrameric structure questionable when compared with the results of the alcohol exchange reactions of the methoxide nickel cubane which seemed to indicate that the eight-membered cubane unit seemed to be relatively inert. However, recent studies of the alkoxide magnesium cubane (20) indicate that this complex disproportionates relatively easily when added to methylene chloride; it precipitates crystals of $Mg(C_5H_7O_2)\cdot 2H_2O$, discussed earlier in this chapter and forms $Mg(OCH_3)_2$ in solution.

A system that appears to be very similar to the previously discussed Ni(EIA) system was prepared with the ligand SALPA, where SALPA is used to represent the dianion of the imine formed from salicylaldehyde and 3-amino-1-propanol. The preparation of $Ni(C_{10}H_{11}NO_2)(C_2H_5OH)$ and $Ni(C_{10}H_{11}NO_2)$ are described in the experimental section; if the preparation of $Ni(C_{10}H_{11}NO_2)(C_2H_5OH)$ is carried out using 95 per cent ethanol instead of absolute alcohol, the complex $Ni(C_{10}H_{11}NO_2)(H_2O)$ is prepared. A thermal gravimetic analysis investigation showed that the $Ni(C_{10}H_{11}NO_2)(H_2O)$ complex lost 7.093 per cent of its weight at approximately 118°C; the calculated per cent weight loss for the loss of water from this complex is 7.098 per cent. Also in this system if the methanolate is added to toluene or xylene and heated the solution turns red.

Due to the similarity between these systems, $Ni(C_{10}H_{11}NO_2)$ may have a dimeric structure like $[Ni(EIA)]_2$; since in the SALPA compound the aminoalcohol portion of the ligand contains three carbons it may be possible for the dimer to be planar through the easing of steric

limitations.

In the case of the planar arrangement, like the $[Cu(PIA)]_2$, three of the four outer orbitals of each bridging oxygen (2s, $2p_x$ and $2p_y$) are used for σ-bonding and the fourth orbital ($2p_z$) is available for π-bonding with the metal d_{xz}, d_{yz} orbitals; in the case of the nonplanar dimer, the fourth orbital does not have π-symmetry.

It seems significant that for all of the oxygen-bridged copper(II) complexes with normal magnetic moments at room temperature, structure studies (7,9,64,65) have indicated tetrahedral hybridization of the outer orbitals of oxygen and π-bonding is not possible.

Structure of $[Cu(C_8H_{10}N_2O)]_2$

In order to investigate further the effect of factors such as ring size and the extent of delocalization on structure and magnetic properties, a complex, $[Cu(C_8H_{10}N_2O)]_2$, was prepared with a five-membered unsaturated ring and a six-membered saturated ring.

Figure 6 shows a perspective drawing of the structure. Table 19 gives bond distances and bond angles. This structure is dimeric and contains a central four-membered ring which, because of an inversion center at the center of the ring, is exactly planar. The maximum deviation of the copper coordination from planarity is the N2 atom which is out of the metal-oxygen plane by 0.191Å (Table 20). The angles at copper are not the 90° angles expected for square-planar coordination but reflect the effect of ring size -- the larger N-Cu-O angle, 106.0(4)°, is not included in a ring, the other N-Cu-O angle, 95.2(4)°, is in the six-membered chelate ring, the N-Cu-N angle, 83.2(5)°, is in

the five-membered chelate ring, and the O-Cu-O angle, 76.1(4)°, is in the four-membered copper-oxygen ring. The coordination around the bridging oxygen is essentially planar, with the carbon bonded to the oxygen only 0.053Å out of the plane of the four-membered ring.

In addition to the four-membered ring, there are three other rings: a six-membered chelate ring, a five-membered chelate ring and a five-membered pyrrole ring. The six-membered chelate ring contains copper, oxygen, three carbons and a nitrogen. The non-metallic parts of the ring all originate from the 3-amino-1-propanol (saturated chelate ring) and C2 is puckered out of the general plane of the molecule (Figure 6 and Table 20). The five-membered chelate ring consists of a copper, two nitrogens and two carbons; the other five-membered ring contains five carbon atoms which originate from the Pyrrole-2-carboxaldehyde. The two five-membered rings are almost exactly planar, with the maximum deviation being the copper which is only 0.030Å out of the least-squares plane (Table 20). All bond distances are very close to previously reported average bond distances (51). The copper-copper distance was found to be 3.001(4)Å (Table 19).

The saturated chelate ring is, as expected, nonplanar. As indicated previously, the carbon bonded to the bridging oxygen is in the plane of the four-membered ring, and the puckered carbon, C2, is the only atom of the entire structure that causes the molecule to deviate significantly from planarity. It is 0.644Å from a least-squares plane defined by all the atoms of the two five-membered rings (Table 20).

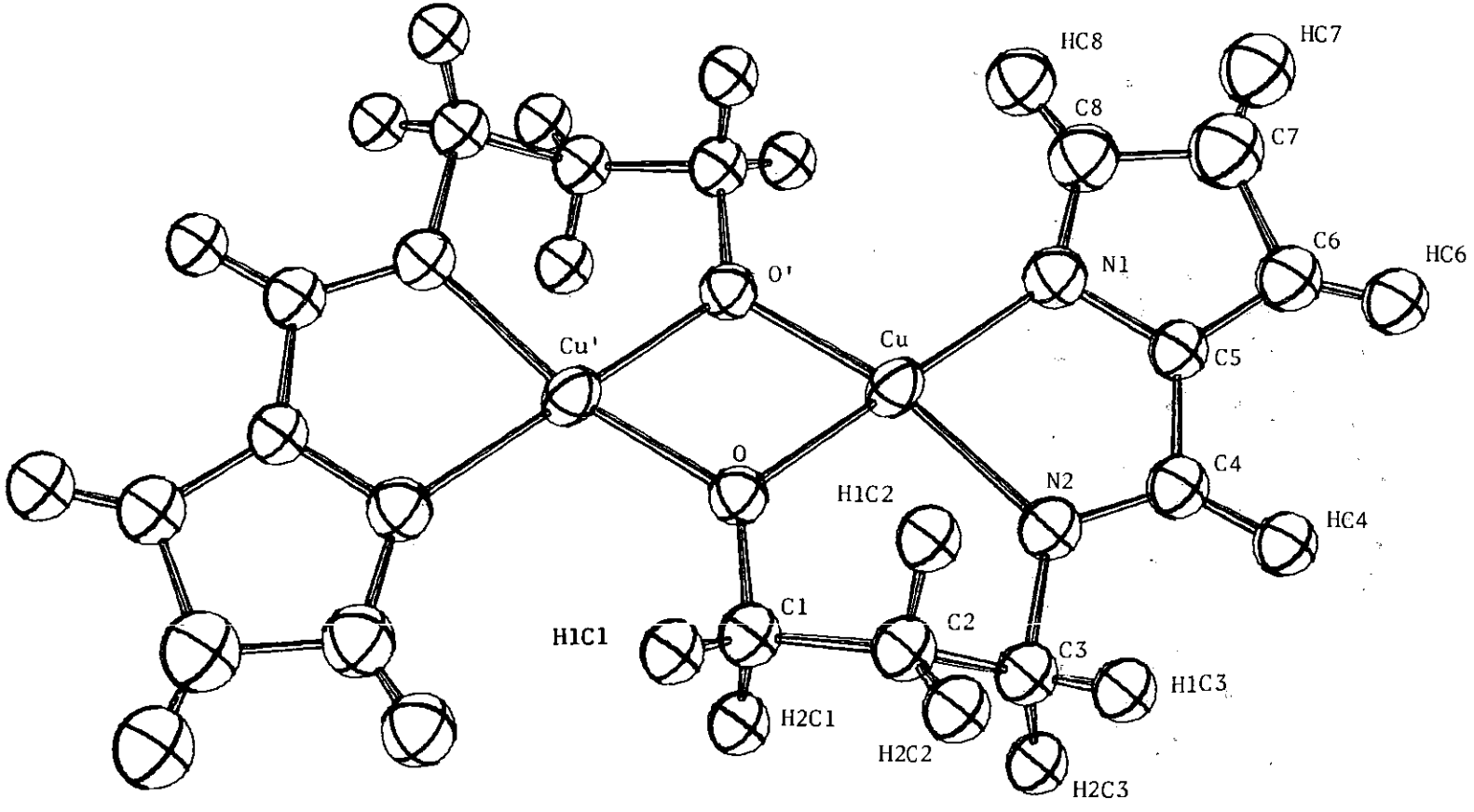


Figure 6. A Perspective Drawing of the Structure of $[Cu(C_8H_{10}N_2O)]_2$

Table 19. Interatomic Distances and Angles for $[Cu(C_8H_{10}N_2O)]_2$

Atoms	Distance, Å	Atoms	Angle, degrees
Cu-Cu'	3.001(4)	Cu-N1-C5	110.7(9)
Cu-O	1.920(11)	C5-N1-C8	106.9(12)
Cu-O'	1.891(7)	Cu-N1-C8	142.2(9)
Cu-N1	1.942(13)	N1-C8-C7	111.1(11)
Cu-N2	1.952(9)	C6-C7-C8	103.7(14)
O-C1	1.435(13)	C5-C6-C7	107.0(12)
N1-C5	1.328(14)	N1-C5-C6	111.3(11)
N1-C8	1.353(18)	N1-C5-C4	117.4(13)
N2-C3	1.472(16)	C4-C5-C6	131.3(11)
N2-C4	1.293(20)	N2-C4-C5	115.4(10)
C1-C2	1.543(20)	Cu-N2-C4	113.0(8)
C2-C3	1.499(15)	Cu-N2-C3	124.5(9)
C4-C5	1.420(17)	C3-N2-C4	122.4(9)
C5-C6	1.379(24)	N2-C3-C2	109.9(9)
C6-C7	1.414(16)	C1-C2-C3	111.3(9)
C7-C8	1.410(23)	O-C1-C2	111.2(13)
C1-H1C1	0.97	Cu-O-C1	126.4(7)
C1-H2C1	1.03	Cu-O-Cu'	103.9(4)
C2-H1C2	0.95	C1-O-Cu'	129.6(9)
C2-H2C2	1.08	O-Cu-N2	95.2(4)

Table 19. (Continued)

Atoms	Distance, Å	Atoms	Angle, degrees
C3-H1C3	0.96	N1-Cu-N2	83.2(5)
C3-H2C3	0.97	N1-Cu-O'	106.0(4)
C4-HC4	1.10	O-Cu-O'	76.1(4)
C6-HC6	1.03	O-C1-H1C1	114.2
C7-HC7	1.01	H1C1-C1-H2C1	105.6
C8-HC8	1.03	C2-C1-H2C1	101.3
		C1-C2-H1C2	141.2
		H1C2-C2-H2C2	93.1
		C3-C2-H2C2	104.0
		C2-C3-H1C3	114.8
		H1C3-C3-H2C3	109.3
		N2-C3-H2C3	103.9
		N2-C4-HC4	127.7
		C5-C4-HC4	116.8
		C5-C6-HC6	133.0
		C7-C6-HC6	119.9
		C6-C7-HC7	138.8
		C8-C7-HC7	117.3
		C7-C8-HC8	116.5
		N1-C8-HC8	131.8

Table 20. Equations of Least-Squares Atomic Planes and Distances of Atoms(Å) from these Planes for $[Cu(C_8H_{10}N_2O)]_2$

(a) Equation of the Least-Squares Plane Including (Cu,O,Cu'):

$$0.216X - 0.435Y - 0.874Z = 0.791$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Cu	0.000	C4	0.201
O	0.000	C5	0.070
N1	-0.086	C6	0.063
N2	0.191	C7	-0.134
C1	0.053	C8	-0.215
C2	-0.302	Cu'	0.000
C3	0.275	O'	0.000

(b) Equation of the Least-Squares Plane of the Coordination Sphere (O,N1,N2,O'):

$$0.205X - 0.410Y - 0.888Z = 0.749$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Cu	-0.032	C4	-0.069
O	-0.039	C5	-0.012
N1	-0.114	C6	0.016
N2	0.072	C7	-0.153
C1	-0.042	C8	-0.205
C2	-0.454	Cu'	0.043
C3	-0.109	O'	0.051

Table 20. (Continued)

(c) Equation of the Least-Squares Plane of the Pyrrole Ring (N1,C5,C6,C7,C8):

$$0.179X - 0.362Y - 0.915Z = 0.470$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Cu	0.068	C4	-0.034
O	0.035	C5	-0.005
N1	0.003	C6	0.005
N2	-0.009	C7	-0.003
C1	-0.091	C8	-0.000
C2	-0.623	Cu'	0.290
C3	-0.078	O'	0.323

(d) Equation of the Least-Squares Plane Including (Cu,N1,C5,C4,N2):

$$0.175X - 0.397Y - 0.901Z = 0.495$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Cu	0.012	C4	-0.001
O	-0.052	C5	0.014
N1	-0.021	C6	0.047
N2	-0.007	C7	0.008
C1	-0.160	C8	-0.030
C2	-0.660	Cu'	0.149
C3	-0.068	O'	0.213

Table 20. (Continued)

(e) Equation of the Least-Squares Plane Including (Cu,N2,C4,C5,C6,C7,C8,N1):

$$0.177X - 0.384Y - 0.906Z = 0.494$$

Atom	Distance from Plane, Å	Atom	Distance from Plane, Å
Cu	0.030	C4	-0.014
O	-0.021	C5	0.004
N1	-0.016	C6	0.027
N2	-0.008	C7	-0.002
C1	-0.133	C8	-0.025
C2	-0.644	Cu'	0.198
C3	-0.070	O'	0.249

As in other polynuclear structures in which the coordination of the bridging oxygen is planar, the room temperature magnetic moment (0.54 B.M.) is considerably below the value expected for one unpaired electron per copper. An explanation of the spin-coupling in such systems in terms of a delocalized π-system involving the $3d_{xz}$ and $3d_{yz}$ orbitals of the coppers and the $2p_z$ orbitals of the oxygens has been suggested. A molecular orbital treatment of these six orbitals indicates two anti-bonding orbitals of different symmetries; since these orbitals can, thus, have different energies, it is possible for the dimer to have a singlet ground state and a thermally accessible triplet state.

Although the energy difference between the anti-bonding π-orbitals of $[Cu(C_8H_{10}N_2O)]_2$ could result from interactions with the chelate π-system, the reason for an energy difference between the corresponding π-orbitals of complexes such as $[Cu(PyO)Cl_2]_2$ (where PyO represents pyridine-N-oxide), which also exhibit sub-normal magnetic moments at room temperature (66), was not apparent from the previous treatment. Furthermore, planar four-membered rings are also present in chloride-bridged complexes of copper(II) and the room temperature moments of those compounds are normal. A review of the available structure data on oxygen-bridged (7,8,9,10,11,24,35,63,64,67,68,69,71) and chloride-bridged (69,72,73,74,75,76) complexes of copper(II) reveals an important difference: in all of the oxygen-bridged complexes with sub-normal room temperature magnetic moments the O-Cu-O angles within the four-membered ring are considerably less than 90° (usually near

70°); in the chloride-bridged complexes the Cℓ-Cu-Cℓ angles approach 90°. By incorporating these observations into the treatment of the pπ-dπ system, it is possible to give an explanation of the energy difference between the anti-bonding orbitals in all of the oxygen-bridged copper(II) complexes that show sub-normal room temperature magnetic moments. The treatment employed has been presented previously (77,78,79) in a general treatment of pπ-dπ systems but has not been applied to transition metal complexes.

Although the actual symmetry of the complexes is usually lower, the four-membered ring in several of the low-moment compounds approached D_{2h} symmetry. Using the coordinate system previously suggested (77), the six π-orbitals, Figure 7, transform in D_{2h} symmetry as $A_u + B_{2g} + 2B_{1u} + 2B_{3g}$; suitable combinations of atomic orbitals which transform with these symmetries are indicated in Figure 8. Of these, the A_u and B_{2g} combinations are non-bonding and there are bonding and anti-bonding combinations with both B_{1u} and B_{3g} symmetries.

Consideration of the B_{1u} and B_{3g} combinations indicates that the two would have identical overlap of copper and oxygen orbitals for an O-Cu-O angle of 90°; however, as the O-Cu-O angle is decreased, the overlap of the B_{1u} combination is increased and that of the B_{3g} combination is decreased. For an O-Cu-O angle of 90°, the B_{1u} and B_{3g} anti-bonding orbitals would, therefore, have the same energy unless they were affected by other factors such as different interactions with a chelate π-system.

In addition to the dependence on the angle at copper, the energy

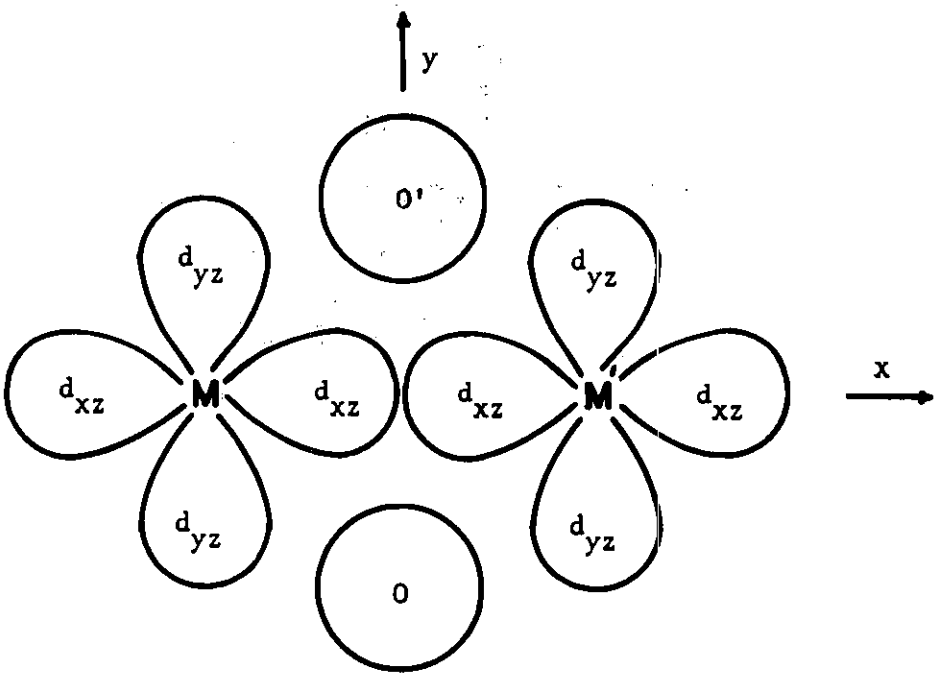


Figure 7. Orbitals of the π-system as viewed down the z-axis.

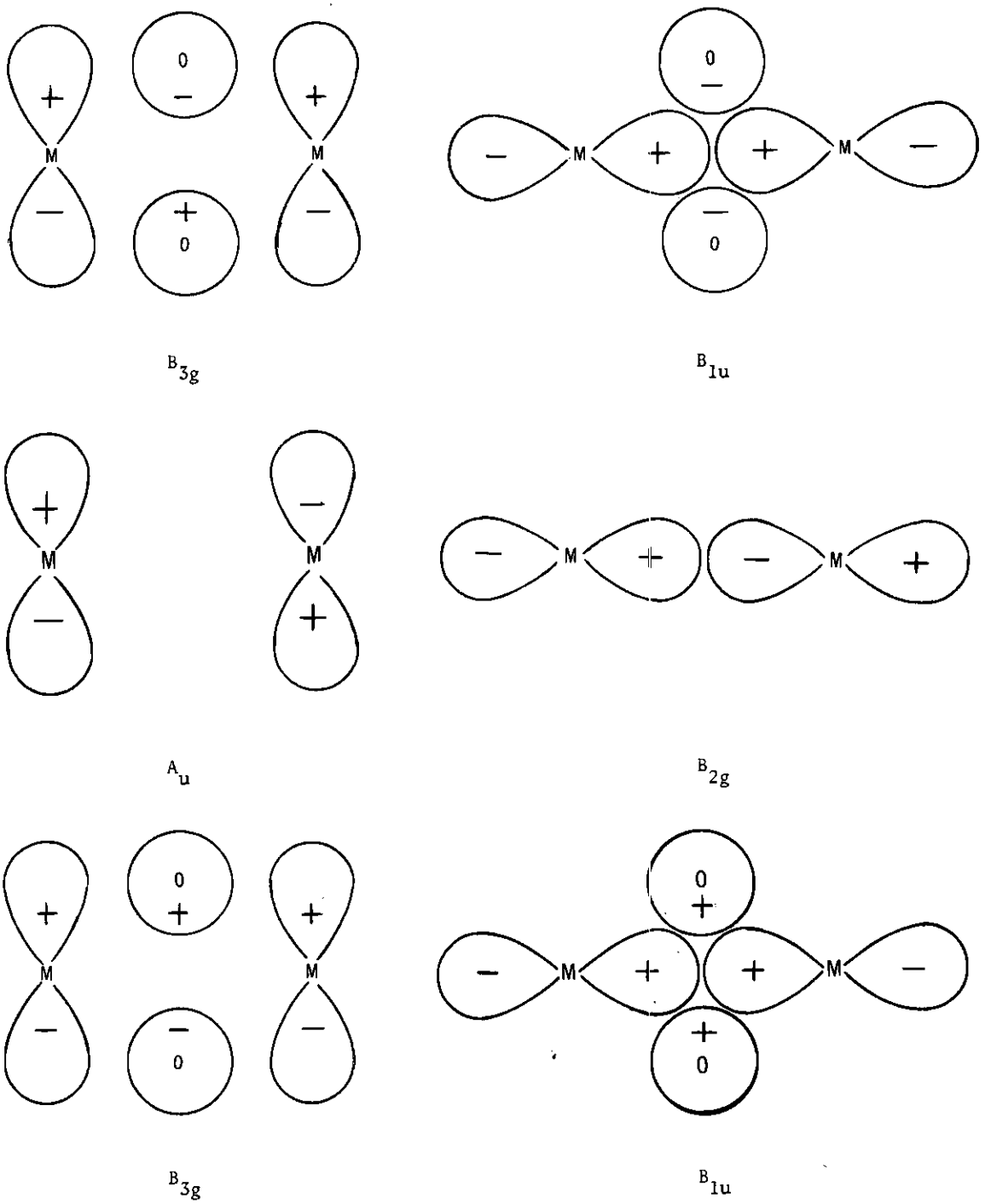


Figure 8. Symmetry Adapted Linear Combinations of Atomic Orbitals

separation would depend on the energies of the oxygen orbitals and the copper orbitals and, since these energies depend on the bonding to the rest of the molecule, the nature of the rest of the molecule would affect the magnitude of the energy difference. This factor is reflected in the variation of the coupling constant, J, with the electron density at oxygen as observed (80) for a series of complexes with substituted pyridine oxides as bridging groups; it also accounts for the difference in magnetic moments observed for compounds such as, $[Cu(C_8H_{10}N_2O)]_2$ and $[Cu(PyO)C\ell_2]_2$, both of which have O-Cu-O angles of 72° to 76°.

In addition to the fact that the above treatment qualitatively explains the observed magnetic moments of oxygen-bridged copper(II) complexes, it is possible to show that such a treatment gives singlet-triplet separations of the right magnitude. Experimental values are available -- the temperature dependence of the magnetic susceptibilities of a number of oxygen-bridged copper(II) dimers have been studied (80,81,82) and have been found to fit the equation (83):

$$\chi_M = (2g^2\beta^2N / 3kT)[1 + \frac{1}{3}\exp(J / kT)]^{-1} + N\alpha$$

where χ_M is the molar susceptibility of the dimer, g is the Lande factor, β is the Bohr magneton, N is Avogadro's number, k is the Boltzmann constant, $N\alpha$ is the temperature independent paramagnetism, and J is the singlet-triplet energy separation. Values for J have usually been less than 500 cm^{-1}; from the room temperature susceptibility of $[Cu(C_8H_{10}N_2O)]_2$ (0.54 B.M.), a J value of approximately 560 cm^{-1} is

obtained.

For purposes of energy calculations, it is convenient to write B_{1u} orbitals in terms of separate oxygen and copper orbitals:

$$\phi_1(B_{1u}) = (p_z + p_z') / \sqrt{2}$$
$$\phi_2(B_{1u}) = (d_{xz} + d_{xz}') / \sqrt{2}.$$

In terms of the general treatment (77,78), these correspond to $\phi_0{}^A$ and $\phi_0{}^B$. Using a Huckel approximation with the following definitions,

$$H_{11} = \int\phi_1 H\phi_1 d\tau = \int p_z H p_z d\tau = \alpha$$
$$H_{22} = \int\phi_2 H\phi_2 d\tau = \int d_{yz} H d_{yz} d\tau = \alpha_{yz}$$
$$H_{21} = H_{12} = \int\phi_1 H\phi_2 d\tau =$$
$$\tfrac{1}{2}\int(p_z + p_z')H(d_{yz} + d_{yz}')d\tau = 2\int p_z H d_{yz} d\tau = 2\beta_{yz},$$

the secular equation is

$$\begin{vmatrix} \alpha - E & 2\beta_{yz} \\ 2\beta_{yz} & \alpha_{yz} - E \end{vmatrix} = 0$$

and

$$E = \tfrac{1}{2}(\alpha + \alpha_{yz} \pm [(\alpha - \alpha_{yz})^2 + 16\beta_{yz}{}^2]^{\frac{1}{2}}).$$

For the B_{3g} orbitals, the appropriate linear combinations of oxygen and copper orbitals are:

$$\phi_1(B_{3g}) = (p_z - p_z') / \sqrt{2}$$
$$\phi_2(B_{3g}) = i(d_{xz} - d_{xz}') / \sqrt{2}.$$

In terms of the general treatment (77,78), these correspond to ϕ_1^A and ϕ_1^B. Using the same definitions as before, the secular equation may be written:

$$\begin{vmatrix} \alpha - E & 2i\beta_{xz} \\ -2i\beta_{xz} & \alpha_{xz} - E \end{vmatrix} = 0$$

and

$$E = \tfrac{1}{2}(\alpha + \alpha_{xz} \pm [(\alpha - \alpha_{xz})^2 + 16\ \beta_{xz}^2]^{\frac{1}{2}}).$$

The energy difference, J, for the two anti-bonding orbitals is given by:

$$J = \tfrac{1}{2}([(\alpha - \alpha_{yz})^2 + 16\ \beta_{yz}^2]^{\frac{1}{2}} - [(\alpha - \alpha_{xz})^2 + 16\ \beta_{xz}^2]^{\frac{1}{2}}).$$

Although α_{xz} and α_{yz} may differ due to interactions with the rest of the molecule, the difference in most compounds is probably not very large and we have used $\alpha_{xz} = \alpha_{yz} = \alpha_d$; however, for an O-Cu-O angle other than

90°, different values are necessary for β_{xz} and β_{yz}. Although there is considerable question about the numerical values to be used, we have used valence state ionization energies (84) for the α's; for the β values, we have used

$$\beta = S_{ij}(\alpha + \alpha_d)\cos\gamma$$

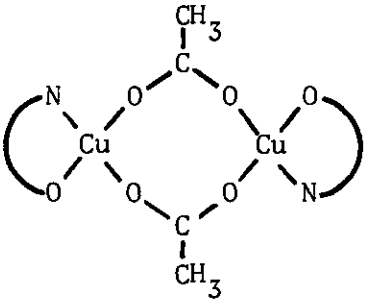
where γ is the angle between the Cu-O direction and the plane of the d orbital; the cos γ term was included (85) to account for the angular dependence of the overlap. The overlap integral was obtained from tabulated values in the literature. With these values we calculate a J value (approximately 870 cm^{-1}) which is of the same magnitude as the observed values.

It thus appears that the low room temperature magnetic moments of oxygen-bridged copper(II) complexes can be explained in terms of a delocalized π-system; it is probable that the same explanation applies to complexes of other metal ions. The same explanation can also be used to explain the low moment observed for CuF_2 since the F-Cu-F angle is 76°.

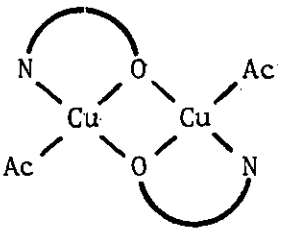
Other Possible Polynuclear Complexes

Another copper complex, $Cu(NH_2CH_2CH_2CH_2O)(CH_3CO_2)$, was examined in this work. By the preceding arguments on π-bonding this copper complex is almost definitely a planar oxygen-bridged dimer due to an observed low magnetic moment. Two structures, 6 and 7, can be proposed that would account for the low moment. At this time, the compound

cannot be completely characterized but it is unlikely to be any more than a dimer.

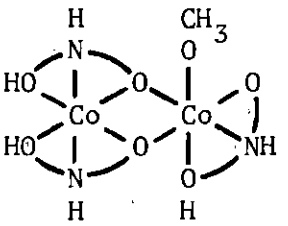


6



7

The complex, $Co_2(C_4H_{10}NO_2)_3(OCH_3)$(I), where $C_4H_{10}NO_2$ is the anion of diethanolamine, is an interesting example where the magnetic properties and elemental analysis were used to characterize the compound. The complex was prepared by a variation of the method of Hieber and Levy (37); 8 analogous to that suggested by Hieber and Levy is a possible structure of this complex.



8

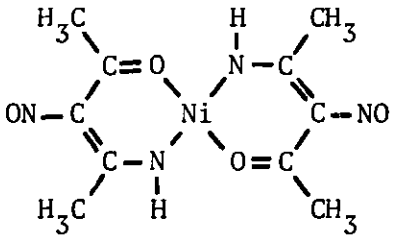
There is no way of knowing at the present where the protons are in this molecule; the missing proton could be removed from the methanol

to form a methoxide as shown or it could be removed from one of alcohol ends of the ligand. The room temperature magnetic moment of this complex is 4.38 B.M. per dimer, which agrees with that expected for one octahedral Co(II) ion; therefore, the complex can be thought of as containing one Co(II) and one low-spin Co(III). In the proposed structure the octahedral cobalts are edge sharing and the structure involves a four-membered metal-oxygen ring. Due to the ligand configuration the carbons are out of the plane of coordination at oxygen and the oxygen is probably not planar.

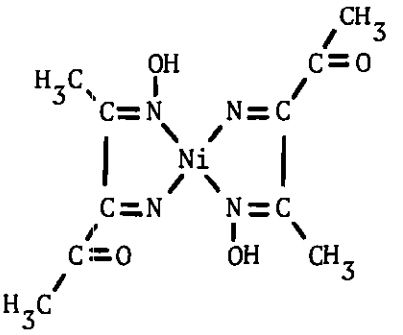
Some ligands may function as bridging groups or as a chelating group on one metal ion; an example is the ligand triethanolamine. A possible bridged structure in which triethanolamine serves as a μ_2 bridge is given by Hieber and Levy (37) for the complex, $[Zn(TEA)(C\ell)]_2$. The green copper complex, $Cu(TEA)_2Br_2$, has a room temperature low magnetic moment, 0.54 B.M., suggesting that the complex exists as a dimer (43). An example was investigated in this study which may be monomeric with the ligand serving only as a chelate group or it may be dimeric. Blue crystals of $Ni(TEA)_2C\ell_2$ were obtained by the preparation of Hughes and Rutt (43); the magnetic moment for the complex is 3.26 B.M. and the complex is probably octahedral Nickel(II).

The complex $NiC_{10}H_{14}N_4O_4$ prepared by the method of Djordevic, Lewis and Nyholm (42) was investigated as an example of an interesting complex with an unusual ligand. The compound is diamagnetic and the observed properties indicate that it is probably square planar. The complex was prepared from nickel acetate, ammonium acetate, potassium

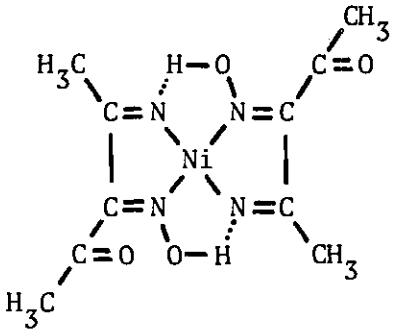
nitrite and acetylacetone; the pH was approximately seven. It was noted by Djordevic, Lewis and Nyholm that attempts to prepare the complex in the absence of ammonia were unsuccessful. An entire set of X-ray date was collected on this complex; however, the interpretation of this data was unclear. Structures No. 1 and No. 2 of Figure 9 were suggested by Djordevic, et al., and No. 3 and No. 4 of Figure 9 are suggested as alternate possibilities. N.M.R. spectra were obtained for this complex in $CDC\ell_3$ solution but the results were inconclusive.



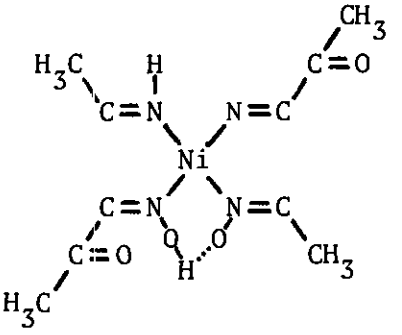
No. 1



No. 2



No. 3



No. 4

Figure 9. Possible Structures for $NiC_{10}H_{14}N_4O_4$

CHAPTER IV

CONCLUSIONS

At the time this work was started cubane structures had been suggested for the methoxide complexes of the general formula $[M(AA)(OCH_3)(ROH)]_4$. The X-ray structure refinement of $[Co(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ is reported in this thesis; also the complex $[Ni(C_5H_7O_2)(OCH_3)(CH_3OH)]_4$ was shown to be completely isostructural with the cobalt complex, and through a joint study with Bell Laboratories (28) the magnetic properties of the nickel cubane as a function of temperature are reported here. Also the complete single-crystal X-ray structure of $[Co(C_5H_7O_2)(OCH_3)(H_2O)]_4$ is reported; this structure resembles the two above cubanes, but the acetylacetonate rings are disordered. While this work was in progress the structure of a similar cubane, $[Ni(sal)(OCH_3)(C_2H_5OH)]_4$, was published (19) by Andrew and Blake.

In these cubanes the four metal ions of one molecule form a tetrahedron; a methoxide ion is located over each face of the tetrahedron with the methoxide oxygen approximately equidistant from the three metal ions defining the face. The two oxygens of an acetylacetonate group and the oxygen of a methanol or water complete the slightly distorted octahedral coordination of the metal ions.

The nickel cubane provided an interesting opportunity to study spin-spin interactions in a crystal lattice composed of nickel tetra-

hedra which are magnetically isolated from neighboring clusters by the peripheal ligands. The temperature dependent magnetic studies indicate that the eight e_g electrons centered on the nickel tetramer are ferromagnetically coupled; the ground molecular spin state for the tetramer is S' = 4, and the ground state is fully populated at 21°K. At even lower temperatures μ_{eff} continues to increase; this indicates that the tetramer molecules in their ground state exhibit an additional intermolecular ferromagnetic coupling. This complex provides the first example of a cluster complex found to exhibit both intramolecular and intermolecular ferromagnetic spin coupling.

The effect of varying the metal ion and ligand in polynuclear complexes has been investigated. The EIA and PIA ligands produce an additional steric restraint on the complexes that is not there in the acetylacetone-methoxide cubanes. The complex, $[Co(EIA)]_4$, prepared in this work, was found to be isostructural with $[Cu(EIA)]_4$ prepared by J. A. Kelley (36,63) and, thus, has a cubane-type structure. The X-ray structure (41) of $[Ni(EIA)]_2$ is presented here. When this work was started there was no example of a metal-oxygen four-membered bent ring in the first transition series. The structure of $[Ni(EIA)]_2$ consists of oxygen-bridged dimers with square-planar coordination about the nickel; the four-membered nickel-oxygen ring is considerably bent. With the ethanolimine ligand it is impossible to have a planar four-membered metal-oxygen ring and square-planar coordination of the metal.

In order to investigate further the effect of factors such as ring size and the extent of delocalization on the structure and magnetic

properties, a complex, $[Cu(C_8H_{10}N_2O)]_2$, was prepared with a five-membered unsaturated ring and a six-membered saturated ring. The compound is a planar dimer with a low magnetic moment of 0.54 B.M. A possible semi-quantitative explanation of the low moment is proposed. The explanation utilizes the O-M-O angle of the planar four-membered metal-oxygen ring to explain the lowering of the moment through the $p\pi$-$d\pi$ system of the metal-oxygen ring.

APPENDIX

The following is an unpublished Algol data reduction program written for use on the Univac 1108 computer. In the following listing a dollar sign ($) is used in place of the standard Algol semicolon.

```
COMMENT THIS PROGRAM IS BY KIRKWOOD FOR USE ON UNIVAC 1108.THIS PROGRAM
        TAKES CONTROL CARDS AND DATA CARDS FROM THE PICKER AUTOMATED
        DIFFRACTOMETER AS INPUT.IT CORRECTS FOR BACKGROUND AND
        CALCULATES THE STANDARD DEVIATION.IT AVERAGES ANY REFLECTIONS
        READ MORE THAN ONCE OR IT CAN AVERAGE ANY SYMMETRY RELATED
        REFLECTIONS WITH A PATCH.CARDS FROM THE DIFFRACTOMETER CAN BE
        INPUT IN SHUFFLED ORDER,IT SORTS AND ORDERS THE OUTPUT CARDS.
        IT OUTPUTS CARDS IN A FORMAT FOR INPUT INTO ZALKINS FORDAP.
           THE CONTROL CARD CONTAINS MIN AND MAX VALUES OF THE INDICES,
        R EQUAL TO SCAN TIME / TIME TO COLLECT ONE SIDE OF BACKGROUND,
        P VARIABLE TO AVOID GIVING STRONG REFLECTIONS UNREASONABLY HIGH
        WEIGHTS,SC A CUT OFF VALUE FOR STD DEV / CORR INT FOR
        REFLECTION TO BE USED.DATA DECK MAY HAVE A 9 IN COL 1 AS A
        FLAG (OPTIONAL).
INTEGER HN,HX,KN,KX,LN,LX,KTR,BI,BII,I,D,H,K,L,C,NN$
REAL CI,RI,RBI,RBII,R,P,SC,SIG,SIGSQ,IW$
FORMAT FA(A,I1,3I3,X25,I1,3I6),
       FD(I1,3I3,X25,I1,3I6,A1),
       FB(3I5,D15.5,D10.5,X31,I1,A1),
       FC(A,6I5,3D10.5)$
LIST AL(C,H,K,L,D,I,BI,BII)$
LIST CL(HN,HX,KN,KX,LN,LX,R,P,SC)$
        READ(CARDS,FC,CL)$
   WRITE('HN=',HN,'HX=',HX,'KN=',KN)$
   WRITE('KX=',KX,'LN=',LN,'LX=',LX)$
   WRITE('R=',R,'P=',P,'SC=',SC)$
        BEGIN
   LOCAL LABEL  WITE,BAD$
REAL ARRAY A(HN:HX,KN:KX,LN:LX)$
REAL ARRAY B(HN:HX,KN:KX,LN:LX)$
REAL ARRAY S(HN:HX,KN:KX,LN:LX)$
INTEGER ARRAY E(HN:HX,KN:KX,LN:LX)$
INTEGER ARRAY F(HN:HX,KN:KX,LN:LX)$
LIST BL(H,K,L,A(H,K,L),S(H,K,L),E(H,K,L))$
        FOR L = (LN,1,LX) DO
        FOR K = (KN,1,KX) DO
        FOR H = (HN,1,HX) DO BEGIN
   A(H,K,L) = 0.00000$
   B(H,K,L) = 0.00000$
   S(H,K,L) = 0.00000$
   E(H,K,L) = 0$
   F(H,K,L) = 0$
        END INITIALIZE$
   WEED:READ(CARDS,FA,AL,WITE,BAD)$
        IF ( C NEQ 1 ) AND ( C NEQ 9 ) THEN NN = NN + 1$
```

```
   GO TO NEXT$
   BAD: WRITE('THIS CARD IN ERROR')$
   NEXT: WRITE(FD,AL)$
        IF C EQL'9 THEN GO TO WITE$
   I = I * 10$ RI = REAL(I)$
   BI= BI * 10$ RBI = REAL(BI)$
   BII = BII * 10$ RBII = REAL(BII)$
        IF (0.5*R*(RBI+RBII) GEQ REAL(I)) THEN GO TO WEED$
   CI = (RI) -(0.5 * R * (RBI + RBII))$
   SIGSQ = (RI + (0.25 * R * R * (RBI + RBII))$
   SIG = SQRT(SIGSQ)$
   IW = SIGSQ / CI$
   WRITE('CI=',CI,'SIG=',SIG)$
   WRITE('SIGSQ=',SIGSQ,'SIG/CI=',SIG/CI)$
   IF (C EQL 1) OR ((SIG/CI) GTR (SC)) THEN GO TO WEED$
COMMENT FOLLOWING LOOP IS PATCH TO AVERAGE SYMMETRY RELATED REFLECTIONS
        THIS MUST BE CHANGED FOR EACH STRUCTURE$
        IF (L EQL 0) THEN BEGIN
   H = ABS(H)$
        END$
COMMENT THE FOLLOWING SCALES FOR THE CALIBRATED ATTENUATORS$
        IF (D EQL 1) THEN CI = CI * 2.7448$
        IF (D EQL 2) THEN CI = CI * 10.0240$
        IF (D EQL 3) THEN CI = CI * 29.6600$
   E(H,K,L) = (((F(H,K,L)) * (E(H,K,L))) + D ) /
              (F(H,K,L) + 1)$
   F(H,K,L) = F(H,K,L) +
   A(H,K,L) = (((B(H,K,L)) * (A(H,K,L))) + CI) /
              (B(H,K,L) + 1.0000)$
   S(H,K,L) = (((B(H,K,L)) * (S(H,K,L))) + IW) /
              (B(H,K,L) + 1.0000)$
   B(H,K,L) = B(H,K,L) + 1.0000$
        GO TO WEED$
   WITE: FOR L = (LN,1,LX) DO
         FOR K = (KN,1,KX) DO
         FOR H = (HN,1,HX) DO BEGIN
   IF ABS(A(H,K,L)) GTR 0.0001
        THEN BEGIN KTR = KTR + 1$
   WRITE(FB,BL)$
   WRITE(PUNCH,FB,BL)$ END$ END$
        END INSIDE$
   WRITE('TOTAL NUMBER COLLECTED =',NN)$
   WRITE('NUMBER OF NONZERO=',KTR)$
        END OF DATA REDUCTION PROGRAM$
```

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